SURFACE MODIFICATION OF FIBROUS FILTER MEDIA TO ENHANCE FILTRATION EFFICIENCY

By

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by

Peter Kea Kang

This Ph.D. dissertation is dedicated with all my heart to my parents who have risked their lives to bring us from the Killing Fields of Cambodia to the United States so that we can get an education. Their courage and hard work in their struggle to succeed in a country where they don't speak the language have truly inspired me and given me strength to do my very best. Without their sacrifice and support, none of this would be possible.

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Abstract of Dissertation Presented to the Graduate School
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SURFACE MODIFICATION OF FIBROUS FILTER MEDIA TO ENHANCE FILTRATION EFFICIENCY

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Fibrous filter media, including microporous polypropylene and microdenier polyester textile fabric, were modified with two types of surface coatings. The first type of modification involved the use of a cationic surfactant, dimethyldioctadecylammonium bromide (DDAB), to make the filter surface positively charged. Negatively charged nanoparticles and biological particles can then be filtered by utilizing the electrostatic interaction between the charged particles and the surfactants adsorbed on the filters. Filtration result for 60 nm negatively charged particles filtered through DDAB treated filter (0.65 μm) shows a significant increase in particle filtration efficiency. Filtration efficiency can be increased from 10% to 95% by using four layers of the filters. In the filtration of bacteria, the surfactant treated polyester textile fabric filters show improvements in the filter coefficient of 195% to 330%. In the filtration of bacteriophages, improvements in the filter coefficient for MS2 and PRD-1 are 3,270%

and 2,830%, respectively, as compared to untreated filters, while the improvement for ΦX-174 is only 98%. Filtration efficiency or filter coefficient calculations are based on the number of viable microorganisms before and after filtration.

The second type of filter modification utilized metal oxides/hydroxides to change the properties of the filters. Three various iron oxides (goethite, haematite and magnetite) were successfully coated on polyester filters by carefully controlling the reaction conditions. Combinations of iron oxide and aluminum oxide were also used to modify the filters. The metal oxide coated polyester filters have zeta potentials which are more positive than the untreated filters. The wettability of the metal oxide coated filters also increased, leading to lower pressure drops across the filters. The filter coefficients of the iron oxide coated filters show improvements of 22% to 60% in the filtration of bacteria. In the filtration of bacteriophages, goethite has the highest filtration efficiency in filtration of MS2 and PRD-1. Phage ΦX-174 has a very strong affinity for the iron oxide treated surfaces. The mixed iron and aluminum oxide coated filters were more effective than the iron oxide coated filters in the removal of both bacteria and bacteriophages, but they are not as effective as the surfactant treated filters.

CHAPTER 1
INTRODUCTION AND LITERATURE REVIEW

1.1 Waterborne Diseases

Waterborne diseases are important public health issues in both developing and developed countries. Many cases of human infections, caused by waterborne pathogens, have occurred in developed countries such as the United States as well as in developing countries. From 1986 to 1988, close to 26,000 cases of diseases in the United States were attributed to waterborne pathogens (Levine *et al.*, 1991). Since that time, other outbreaks that have occurred in the United States include 34 outbreaks associated with drinking in 17 states and territories from 1991 to 1992 and the Cryptosporidium outbreak in Milwaukee, which caused intestinal disease in over 400,000 people. The most common illness associated with waterborne diseases is gastroenteritis. Other reported water - associated illnesses include pneumonia, typhoid fever, hepatitis, mycobacteriosis, leptospirosis, and dermatitis (Levine *et al.*, 1991; Sherris *et al.*, 1990).

Although outbreaks continue to occur in developed countries, the number of outbreaks has been greatly reduced with the use of disinfectants as the final step in water treatment facilities. However, the use of chlorine to treat drinking water does have some disadvantages. Some of these disadvantages or concerns include the harmful byproducts that may be released to the environment or consumed by human. As the standards for water quality become stricter, other more efficient methods to improve the aesthetic and

chemical quality of the water supply must be found. In underdeveloped or developing countries, wastewater treatment facilities are not available to all communities. In most of these communities, the same sources of water are used for drinking, cooking, bathing and cleaning. Under these conditions, outbreaks can spread very quickly. There is a great need for economical water treatment processes in these areas of the world.

1.2 Bacterial Adsorption

Interactions between microorganisms and surfaces have been extensively studied as described below. Unlike colloidal particles, microorganisms are do not behave as "ideal" particles, and therefore, no one has been able to determine exactly the factors that affect microbial adhesion to surfaces. Without knowing which parameters are important, it is difficult to design the perfect filter media. Electrostatic interaction has been reported to be the predominant factor in microbial adhesion to surfaces (Daniels and Kempe, 1966; Daniels, 1980; Lukasik *et al.*, 1996.). Daniels and Kempe (1966) investigated the adsorption-desorption of bacteria (*E. coli, P. ovalis, B. subtilis, S. aureus, B. cereus, P. vulgoris*) onto ion exchange resin particles. They believed that the mechanism of adsorption-desorption was primarily due to the electrostatic interactions. At pH values above their isoelectric points, bacteria have a net negative charge on their cell surface. Ion exchange resins, such as replaceable chloride ions associated with positively charged quaternary ammonium groups were used. The negatively charged bacteria and the positively charged resin particles combined to form flocculated particles. They concluded that the rate and extent of exchange were dependent upon both the pH and the salt content of the solution.

In addition to electrostatic interactions, external factors such as pH, temperature, and ionic strength have been shown to be important factors as well. Adsorption/adhesion of bacteria, generally, occurs at pH 3-pH6 (Easterman and McLaren, 1959; Gunnison and Marshall, 1937; Daniels, 1980). Since the bacterial cells are negatively charged in neutral pH, lowering the pH probably decreased the electronegativity of the cell walls, and therefore, decreased the repulsion between the bacteria and the filter surface. Addition of multivalent cations has also been shown to enhance bacterial adhesion to surfaces. Other factors which have been proposed to explain bacterial adhesion to surfaces include hydration forces (Israelachvili, 1992), hydrophobic interactions (Gerba *et al*, 1981; van Loosdrecht *et al.*; 1987a; van Loosdrecht *et al* 1987b; Stenstrom, 1989), macromolecular bridging (Dickinson, 1997), and surface roughness (Elimelech, 1990; Verheyen *et al.*, 1993).

1.3 Viral Adsorption

Viruses have protein coatings consisting of amino acids. These amino acids may be hydrophobic, basic, or acidic. The ionization of these amino groups contributes to the net charge of the viruses as a function of pH. Electrostatic interaction, hydrophobic interaction, and hydrogen bonding have been reported by Mix (1974) as the important factors controlling viral adsorption to filter surfaces. Farrah and Bitton (1982) and Farrah *et al.* (1991) reported that hydrophobic and electrostatic interactions were essential in viral adsorption to filter surfaces. These interactions depend on the nature of the virus, the composition of filter, the nature of the solution, including the type of salts in the

solution, the presence of organic materials, and the pH of the solution (Mix, 1974; Bitton, 1980).

The type and composition of the filters have a large influence on the adsorption of viruses. Cellulose acetate and cellulose nitrate membranes were effectively used to adsorb viruses (Cliver, 1968; Wallis *et al.*, 1972). The pore size of the filters plays a role as well. At pore sizes close to the diameter of the virus, even materials with low affinity for viruses adsorb large quantities of viruses in the absence of interfering substances. In the presence of interfering compounds, adsorption is significantly decreased. According to Cliver's experiment, the addition of serum reduces the adsorption of viruses to the filters. The interaction between the serum type and the membrane type was not explained. Organic compounds are suspected of interfering with adsorption by competing for adsorption sites on the membrane (Gerba, 1985). Because of this effect, organic compounds have been used to elute viruses from filters. Beef extract, yeast extract, casein, and fetal bovine serum are just some of the solutions that have been used by researchers for eluting viruses from the filter surface.

Surface modifications based on electrostatic interactions have been shown to be very effective in the adsorption of virus. Brown *et al.*(1974) and Preston *et al.* (1988) have shown that adsorption of viruses can be significantly increased with the use of cationic polymers. The increase in adsorption is attributed to the electrostatic attraction between the cationic polymers and the microorganisms. Metallic oxide and hydroxide coatings have also been shown to be very effective in adsorbing viruses. The use of metallic oxides and hydroxides will be discussed in Chapter 5.

Sobsey and Jones (1979) published the first use of electropositive filters in the concentration of poliovirus from tap water. In their research, they compared the efficiency of negatively charged and positively charged filters. The negatively charged filter media composed of fiberglass-asbestos (Cox) and had a 0.45 µm pore size. Two types of positively charged filter media were used. The first composed of asbestos-cellulose and had pore size of 0.5 µm. The second was made from cellulose-diatomaceous earth-"charged-modified" resin, having pore size of 0.45 µm or 0.75µm (Zeta Plus, Type 50S and 60S, respectively). The Cox filters are electropositive up to a pH of about 3.5. The Zeta Plus filters were found to have a higher isoelectric point, and thus are more positively charged around the neutral pH range. From the electrophoretic mobility measurements, they concluded that the Cox filter, which is negatively charged in the neutral pH range, would make a poor filter media since the viruses are also negatively charged, and thus they would repel each other. The more positively charged Zeta Plus filters are better candidates since their isoelectric points are between pH of 5 and 6. The results showed that the Zeta Plus filters are much more effective than the Cox filters as virus adsorbent in the pH range of tap water and natural water. Zeta Plus 50S filters are effective for pH values between 5.5 and 7.5. The optimum pH range for the Zeta Plus 60S is 3.0 to 6.0.

Goyal *et al.* (1980) used the Zeta Plus filters to concentrate coliphages from large volumes of water and wastewater. These positively charged microporous filters were found to be effective in the adsorption of four different coliphages in the neutral pH range. The different coliphages were MS2, ΦX-174, T2, and T4. Research was also done, by the same group, on other filters for comparison purposes. These included anion

exchange filters, cation exchange filters, Acropor SA-6404 with special C-10 resin filters, and Filterite filters. It was shown that the positively charged filters performed much better than the other four filters. The Zeta Plus filters adsorbed phages regardless of whether the suspending media was tap water, distilled water, secondary sewage, glycine solution, river or lake water.

More recently, Shields *et al.* (1986) studied virus adsorption-elution on four different electropositive membrane filters. They used Virosorb 1MDS, Posidyne N66, Zeta plus C-30, and Seitz S filters. The hydrophobicity of these filters was determined by measuring the contact angle of carbon tetrachloride with the filters submerged in water and by evaluating the rate of rise of hexadecane and water in the filters. They discovered that all four types of filters have approximately the same adsorption efficiency for adsorption of phage in tap water. Differences, however, were seen in the elution phase. The differences in the elution of the adsorbed phages were attributed to the differences in the relative strength of the electrostatic and hydrophobic interactions between the phages and the filters. These interactions were found to correlate well with physical parameters such the contact angle of a nonpolar liquid with the filter. In the least hydrophobic filter (Virosorb 1MDS), the elution of the adsorbed viruses was accomplished by adding a salt solution (NaCl or NaEDTA) to disrupt the electrostatic interaction between the viruses and the filter. In the more hydrophobic filters (Posidyne N66 and Zeta plus C-30), solutions containing both salt and detergent were needed to elute the adsorbed phage. This was taken as an indication that electrostatic and hydrophobic interactions were responsible for the adsorption of these viruses to the filters.

1.4 Particle Adsorption

Although all of the factors affecting bacterial and viral adsorption are also applicable to adsorption of non-biological nanoparticles, a brief review of particle filtration literature is provided here. The removal of particulate contaminants is very important in many industries. Some of these industries include water reclamation facilities, potable water treatment, microelectronics and pharmaceutical industries. Filtration of particulate contaminants is dependent on several factors including particle size and physicochemical properties of the particles and the collectors or filter media. Large particles can be filtered by entrapment mechanism. As the size of the particle decreases, however, particle removal becomes more difficult and thus the interaction between the particles and the collectors must be increased to enhance filtration efficiency.

Deposition of submicron particles onto collectors has captured the interest of many investigators over the years (Clint *et al.*, 1973; Fitzpatrick and Spielman, 1973; Spielman and Friedlander, 1974; Rajagopalan and Tien, 1977a, 1977b; Onorato and Tien, 1980; Oak *et al.*, 1985; Shields *et al.*, 1986; Russell *et al.*, 1989; Chang and Vigneswaran, 1990; Sisson *et al.*, 1995; Johnson and Lenhoff, 1996). The main focus of these researches has been on the interactions between the particles and the collectors. The dominant factors in submicron particle adhesion/deposition is the surface interaction forces and Brownian motion (Onorato and Tien, 1980; Russell *et al.*, 1989; Chang and Vigneswaran, 1990). Onorato and Tien (1980) have found that favorable interactions between particles and the collector can significantly increase particle deposition. They reported a ten fold increase in the deposition of negatively charged particles on a

positively charged collector as compared to a negatively charged collector. Chang and Vigneswaran (1990) have shown that by decreasing the electrostatic repulsion between the particle and the filter surface, particle attachment can be greatly enhanced. Harley *et al.* (1992) studied the adsorption of small particles onto larger particles of opposite charge. Their results support the implication that long range interactions play an important role in the amount of particles adsorbed and the rate of adsorption.

1.5 Particle Track Microfilters

Particle track filters were used by Shi-Lun Guo and colleagues (1991) to filter bacteria having different size and shapes. The filter track microfilters were constructed from Makrofol KG foils. The pores of the filters were made by irradiation with fission fragments and with heavy ions. The advantage of the particle track filter over the conventional membrane filter is its uniform pore size in each filter. They studied the filtration of spherical shaped bacteria (staphylococci, 0.8-0.9 μm in diameter), rod-like bacteria (colon bacilli, 1-4 micrometer in length and 0.4-0.7 μm in diameter), and mixed miscellaneous bacteria. They used filters with pore sizes of 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0, and 3.0 μm. Their results showed that the penetrability of staphylococci through the filters decreases steeply as the pore sizes decrease from 1.0 to 0.8 μm. When the pore sizes are larger than the size of staphylococci, the particle track filters were still able to capture some of the bacteria on its surface. When the pore sizes were smaller than the size of the bacteria, very few bacteria passed through the filters. The same results were observed with colon bacilli with the exception that the width of the bacteria is the predominant factor and not the length. When the 0.2 μm pore size filter was used, no

colon bacilli passed through the filter. The penetrability of the mixed bacteria had the same result. The capture efficiency increases with decreasing pore size. No bacteria passed through the filter with pore size of 0.4 μm.

Khan *et al.*(1991) used Kapton sheets that were irradiated with heavy ions and then etched with NaOCl-solution to get the needed size. Their results were in agreement with those of Guo *et al.* (1991).

1.6 Purpose of This Study

In developed countries, waterborne disease outbreaks are greatly reduced due to the improvements and availability of water treatment facilities. The use of disinfectants has also kept the number of outbreaks to a minimal. However, with stricter water quality standards in the coming years and the concerns over harmful byproducts of disinfectants, more efficient filtration media are needed to meet these needs. Sand and diatomaceous earth have been used because of their availability and low cost. Therefore, the most economical and logical solution is to increase the filtration efficiency of these filter media through surface modifications. With this in mind, a group of researchers from the National Science Foundation Engineering Research Center (ERC) for Particle Science & Technology at the University of Florida has been pursuing this objective. The objective is to elucidate the factors controlling microbial adhesion to surface so that more efficient filters can be engineered.

Sand media is best suited in large-scale water treatment facilities but in underdeveloped or developing countries, these facilities may not be available to all communities. Sometimes, due to the size of the community, a water treatment facility

may not be economical. For these reasons, there is a need for economical household water filters. Microporous filters or fibrous media can fill this need. The advantages of fibrous media are their higher surface area and their lightweight so that they can be easily transported. In comparison, most of the cost of sand used in water treatment facilities is the transportation cost. The coated fabric filters for purification of water has many other possible advantages. Troops can carry such filters when they are placed in areas where pure water is not available. And the light weight filters can be transported by air to various parts of the world. These filters can also be used by persons in outdoor activities such hiking, tracking or camping. Other possible uses include resource recovery and air filtration applications.

Review of the literature indicates that surface modifications based on increasing the electrostatic interaction between the particles and filter surface can significantly increase the filtration efficiency of the filters. The objective of this study is to modify the surface of fibrous media to enhance the filtration efficiency in the filtration of bacteria and viruses. To that end, two different types of modifications will be discussed. The first is the novel use of surfactants to lower the energy barrier between the microorganisms and the filter surface so that microbial adsorption can be significantly increased. A cationic surfactant, dimethyldioctadecylammonium bromide (DDAB), was used to modify microporous polypropylene filter and polyester textile fabric filters. The second type of modification involves the use of metal oxides to increase the filtration efficiency of polyester textile fabric filters. The use of metal oxides and hydroxides in the field of filtration has received a great deal of attention in the last decade. However, in all of the research, the different morphologies of the oxides were not identified. The precipitated

oxides were probably mixtures of different forms of oxides. In this study, three different forms of iron oxides were successfully coated on polyester fibers by controlling the reaction conditions. These iron oxides are goethite, haematite, and magnetite. This coating process provided coatings that are unlike any of the treatments seen in literature. The coatings were directly adsorbed on the fibers and therefore, clogging of the filters did not occur. Mixtures of goethite and aluminum oxides mixtures were also successfully coated on polyester fabric. It is hoped that the different oxides will have properties that are more desirable than the mixed oxides obtained by "quick" (uncontrolled) precipitation on the filter surface.

CHAPTER 2
FILTRATION OF NANOPARTICLES WITH SURFACTANT TREATED POLYPROPYLENE FILTERS

2.1 Introduction

The removal of particulate contaminants is very important in many industries. Some of these industries include water reclamation facilities, potable water treatment, microelectronics and pharmaceutical industries. Filtration of particulate contaminants is dependent on several factors including particle size and physicochemical properties of the particles and the collectors or filter media. Large particles can be filtered by entrapment mechanism. As the size of the particle decreases, however, particle removal becomes more difficult and thus the interaction between the particles and the collectors must be increased to enhance filtration efficiency.

The focus of the present study is on the electrostatic attraction between the particles and the fibers of microporous polypropylene filters. A cationic surfactant is used to lower the energy barrier between the particles and the filter surface and thus increase the deposition of these particles on the surface of the filter. Polypropylene is commonly used to make prefilters and filters because it is extremely inexpensive and very inert. Because most natural materials are negatively charged (Davies and Rideal, 1961), the microporous polypropylene filters were modified with a monomolecular layer of cationic surfactant to give it a positive charge. The adsorption of negatively charged

particles on the filters was investigated with scanning electron microscopy. Filtration efficiency of these surface modified filters (Figure 2-1) was also studied.

2.2 Filter Treatment

Filters used in these experiments are melt-blown microporous polypropylene disk filters with a diameter of 25 mm (Millipore, MA). The average pore sizes are 0.6 μm (AN06), 1.25 μm (AN12), 2.5 μm (AN25), 5.0 μm (AN50), and 10.0 μm (AN1H). The average pore diameters were supplied by the manufacturer. These filters were treated with a two-tailed water insoluble cationic surfactant, dimethyldioctadecylammomiun bromide (DDAB), by first dissolving the surfactant in methanol and then soaking the filters in the methanol solution (4 ml per filter) for 3 hours. After the 3-hour treatment, the filters were vacuum dried overnight. Before using them for filtration experiments, the filters were flushed with 30 ml of distilled water to remove excess and/or loose surfactants from the filter surface. Dimethyldioctadecylammonium bromide is purchased from Sigma Chemical Company (St. Louis, MO) and used without further purification.

2.3 Surface Charge and Concentration Measurement of Nanoparticles

The nanoparticles were purchased from Bangs Labs, Inc.(Carmel, IN). The negatively charged particles, P(S/A/V-COOH), composed of polystyrene, an acrylic polymer (unspecified), a vinyl group (unspecified polymerizable group), and a functional carboxylate group. The average diameter and surface charge density of these nanoparticles are 60±3.6 nm and 365 μeq/g, respectively, and 197 nm (no standard deviation given) and 141 μeq/g, respectively. The positively charged particles are quaternary ammonium modified polystyrene particles (P(S/Quat Ammonium)) with an

average diameter of 200 nm and a surface charge density of 121 μeq/g. Particle concentrations (wt% solids) are measured by UV absorbance with a Hewlett Packard 8453 UV/VIS spectrophotometer at a wavelength of 255 nm.

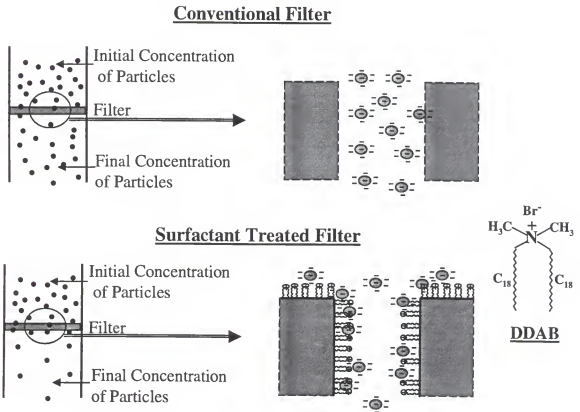


Figure 2-1. Schematic illustration of particle capture in conventional filter and filter coated with a monomolecular layer of surfactant.

2.4 Qualitative and Quantitative Measurement of Surfactant Coating

Qualitative comparison of the degree of DDAB coating on the filters was done through contact angle measurements. AN06 (0.6 μm) filters were treated with different concentrations of DDAB according to the procedure mentioned above. After the filters were rinsed with 30 ml of distilled water, they were cut into four strips. The strips were

then submerged onto a rectangular piece of PMMA (4 mm in thickness) in a 50 ml beaker (Pyrex No. 1000) containing 20 ml of distilled water (Figure 2-2). A drop, approximately 1.5 µl, of 1,1,2,2-tetrabromoethane was placed on top of the filter with a microsyringe. After the droplet was allowed to spread on the filter for 1.5 minutes, the contact angle of the droplet was measured with a contact angle goniometer. Six readings at different locations on the filter surface are taken with each of the filters to get an average contact angle value. Zeta potentials of the filters were measured with a streaming potential apparatus described in the appendix.

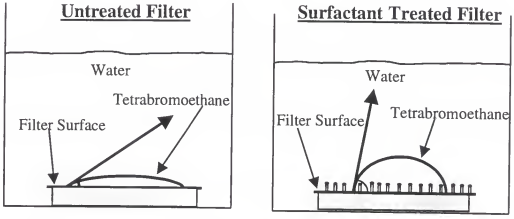


Figure 2-2. Schematic illustrating contact angle measurement for the microporous filters.

The adsorptive capacity of the positively charged surface was estimated by challenging the surface with an anionic dye. This method has been used by other researchers but with different dyes (Knight and Ostreicher, 1981; Jan *et al.*, 1994). The dye used in this experiment was phenol red with a molecular weight of 354.38. The concentration of the dye was 1.25×10^{-4} moles/liter and the flowrate was kept at a constant

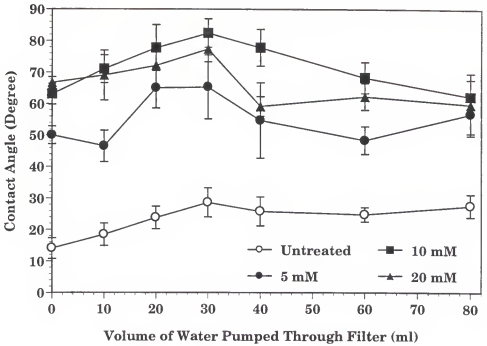


Figure 2-3. Qualitative comparison of the degree of coating and stability of coating by using contact angle measurement for both surfactant treated and untreated AN06 (0.6 μm) filters.

rate of 8.0 ml/minute. Results from the dye challenge experiments for the different DDAB concentration treated AN06 filters are shown in Figure 2-4. The area under the curve for each filter is the amount of dye passed through the filter. The difference between the amount for the untreated filter and the treated filter is assumed to be absorbed by the surface of the filters. Following this logic, it is apparent that a small amount dye adsorbed on the untreated filter and as the surfactant treatment concentration increases, more dye is adsorbed on the surface, indicating a higher positive charge density on the surface. By using this method and assuming that there is a one-to-one complex between the anionic dye molecules and the surfactant molecules, the amount of surfactant

on each filter was calculated to be 0.91×10^{-7}, 1.80×10^{-7}, and 2.94×10^{-7} moles for the 5 mM, 10 mM, and 20 mM DDAB treated AN06 filters, respectively.

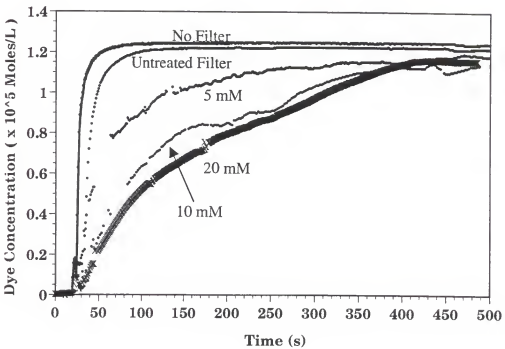


Figure 2-4. A comparison of dye breakthrough curves for no filter, untreated AN06, and 10 mM DDAB treated AN06 filters.

An alternative method to quantify the amount of surfactant adsorbed on the filter surface is to extract the surfactant from the filters with chloroform and then measure the amount of surfactant in solution by spectrophotometric method (Few and Ottewill, 1956). In this method, the Orange II dye, is soluble in the aqueous phase and the surfactant is soluble in the organic phase, but the complex is soluble in the organic phase. Once the surfactant was extracted to the organic phase, the chloroform and the dye solutions were mixed and shaken. Then the solution was allowed to phase separate and the absorbance of the colored organic phase was measured with a UV/Vis spectrophotometer at a wavelength of 485 nm. Results show that 1.36×10^{-7}, 3.07×10^{-7}, and 4.62×10^{-7} moles of

DDAB were extracted from the 5 mM, 10 mM, and 20 mM DDAB treated AN06 filters, respectively. All of the experiments were done in duplicate.

Since the dye challenge method only determines the number of surfactant molecules on the surface, i.e. surface coverage, a comparison with the total amount of surfactant by the chloroform method could give an indication of how the surfactant is adsorbed on the surface of the filters. The fact that the amount of surfactant determined by the dye challenge method can be explained as follows. First, the assumption of a one-to-one association between the dye and surfactant molecule may not be accurate. Secondly, the surfactant molecules may not be present explicitely in a monolayer. If there are surfactant aggregates or multilayers present on the filter, the dye will only react with the molecules on the surface, while the surfactant molecules below the surface will not be detected by the dye.

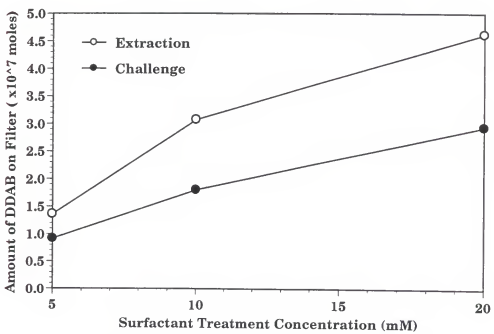


Figure 2-5. Comparison of the amount of surfactant adsorbed on the filter surface as determined by chloroform extraction and dye challenge methods.

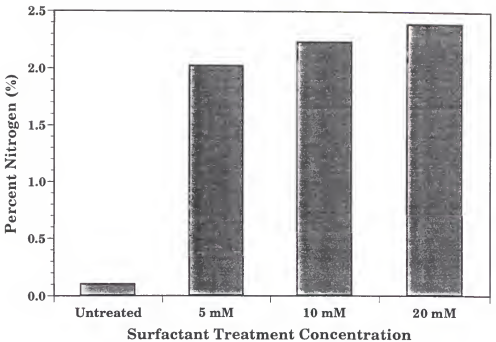


Figure 2-6. Ratio of elemental nitrogen to elemental carbon as determined by XPS.

X-ray photoelectron spectroscopy (XPS) was also used to determine the ratio of nitrogen to carbon on the untreated and surfactant treated filters. The percentages of nitrogen on the surface of the filter are shown in Figure 2-6.

2.5 Filtration Apparatus

Filtration is accomplished by using a stainless steel filter holder, a 12-ml glass syringe and a syringe pump with variable speed control (Dual Infusion/Withdrawal Pump, Model 944, Harvard Apparatus Co., Millis, Mass). For each experiment, 10 ml of particle suspension is filtered through each filter at a constant flow rate of 9 ml/minute. The filtrate was collected in a 11-ml glass vial and then transferred to UV/Vis cell for concentration measurement.

2.6 Adsorption and Desorption of Surfactant from Filters.

Microporous polypropylene filters are coated with a monomolecular layer of dimethyldioctadecylammonium bromide (DDAB) to give them a positively charged surface. DDAB is chosen because of the two hydrocarbon chains that can hydrophobically bond to the surface of the polypropylene and make this surfactant insoluble in water. Contact angle is used as a measure of the amount of DDAB adsorption at the surface of the filters. For smooth, nonporous planar solids, contact angle measurements can be easily accomplished by placing a droplet of liquid such as carbon tetrachloride on the surface of the substrate and measuring the angle by using a microscope fitted with a goniometer eyepiece. For the polypropylene filters, however, contact angle measurements is a little more difficult. First, carbon tetrachloride could not be used because it is too hydrophobic and immediately gets absorbed into the fibers upon contact. The liquid that is suitable for this material is 1,1,2,2-tetrabromoethane. Secondly, the surface of the microporous filter is not smooth. Surface roughness can increase or decrease the contact angle. For wetting surfaces, $\theta < 90°$, surface roughness reduces the contact angle, but increases for non-wetting surfaces (Davies and Rideal, 1961). For this reason, an average of six readings at different locations on the filter surface and the standard deviations are reported in Figure 2-3. High contact angle is an indication that the surface is hydrophilic. Conversely, low contact angle means that the surface is hydrophobic. The average contact angle for the untreated filters is approximately 25°. The 5 mM DDAB solution treated filters have the lowest contact angles among the treated filters and the 10 mM DDAB treated filters have the highest

contact angles (Figure 2-3). Since the standard deviations of these measurements are very large, it was concluded that the difference in 10 and 20 mM DDAB treated filters was not very significant. After examining the SEM pictures, dye analyses, and contact angles, the 10 mM treatment is chosen as the standard method of treatment for the filters.

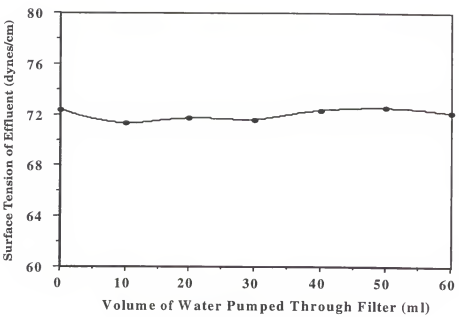


Figure 2-7. Surface tension of rinse water (rinse effluent) after it has been pumped through a 10 mM DDAB treated AN06 filter.

The adsorption strength of the cationic surfactant was tested by flushing the treated filters with different amounts of water and then measuring the contact angles. The amount of water pumped through the filters does not have a significant effect on the contact angle which indicates that the surfactant is not desorbing. The effluents were collected for surface tension measurements (Figure 2-7). The results indicated that the surfactant was not desorbing as detected by surface tension measurements. From previous experiments, we have shown that 2.5×10^{-5} moles/L of the surfactant in water decreased

the surface tension of water from 72.4 to 43.9 dynes/cm. Therefore, surface tension method should be able to detect DDAB in the range of micromoles per liter of water.

2.7 Filtration Efficiency of DDAB Treated Filters

Filtration efficiency or percent removal is significantly enhanced with DDAB treatment. Each of the data points plotted in Figure 2-8, is an average of two runs. For the untreated filters, the filtration efficiency ranges from 5% to 10%, but after the filters were treated with 10 mM DDAB, filtration efficiency increased to 50% or 60% for the lower initial concentration range. The increase in filtration efficiency is mainly due to the electrostatic attraction between the negatively charged particles and the positively charged polar head of the surfactant molecules on the filter surface. Since the average pore size is 0.6 μm, the increase in filtration efficiency is partly due to the smaller pore size in certain regions of the filters due to surfactant adsorption in clusters. However, by examining the results for the filtration at pH 10.0, it is evident that the increase due to entrapment is not very significant since the filtration efficiency of the treated and untreated filters are very similar. If entrapment is the main mechanism, then filtration efficiency should not be dependent on the pH of the suspension unless pH induced flocculation is occuring. However, if pH induced flocculation is taking place, then the filtration efficiency of the untreated filters should increase as pH is lowered. This was not observed experimentally. In adddition, quasi-elastic light scattering measurements showed that the average particle size did not increase with decreasing suspension pH, indicating an absence of flocculation at lower pH.

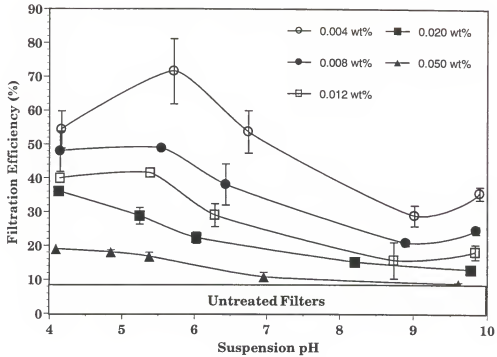


Figure 2-8. Filtration efficiency of 10 mM DDAB treated AN06 (0.6 μm) filters at various initial concentrations of 60 nm P(S/A/V-COOH) and different suspension pH values.

Since the particles are more negatively charged at higher pH values due to a higher degree of ionization, higher filtration efficiency is expected at the higher pH range. However, the results show the opposite trend. Filtration efficiency is higher at the lower pH range. This trend could be due to one of the following two effects. Either the surfactant is desorbing at the higher pH range or competitive ion adsorption is taking place.

To determine if the surfactant is desorbing, the treated filters were flushed with pH 10.0 solution. The effluents were collected for surface tension measurements. If the DDAB is desorbing, then surface tension of the effluents should be lower than the pure water due to the surfactants at the surface. Results indicate that there was no change in

surface tension of the effluents. Further proof that the surfactants are not desorbing is offered by contact angle measurements. Even with 200 ml of pH 10.0 solution flush, the average contact angle of the surface, 70.7±12.7 degrees, remain approximately the same as those that were flushed with 30 ml distilled water. Finally, the filters were rinsed with 30 ml of pH 10.0 solution, followed by 20 ml of distilled water, and then used to filter particles at pH 4.0. Results, as shown in Figure 10, indicate that the filters are just as effective as those that were rinsed with distilled water, which is another indication that the surfactant is not desorbing at the higher pH values.

Since the surfactants are not desorbing, the only other explanation is that the hydroxide ions are competing with the negatively charged particles for the positively charged surfactant sites. At pH 10.0, for example, because of the high number of hydroxide ions and because of their higher mobility due to their smaller size, they can diffuse to the surface of the filter much faster than the large negatively charged particles. The adsorption of the hydroxide ions shields the charge of the surfactants from the particles, and therefore, the particles are not adsorbing to the surface of the filters (Figure 2-12).

In Figure 2-8, the different lines in the plot represents different initial concentrations or solids loading. In terms of percent removal, the higher the initial concentration, the lower the percent removal. This is not to say that the number of particles removed decreased. On the contrary, the number of particles removed from the aqueous stream increased with the increasing initial concentration because more particles were diffusing to the surface and were captured by the surfactants. In Figure 2-10, the results from Figure 2-8 are replotted in terms of the number of particles removed per

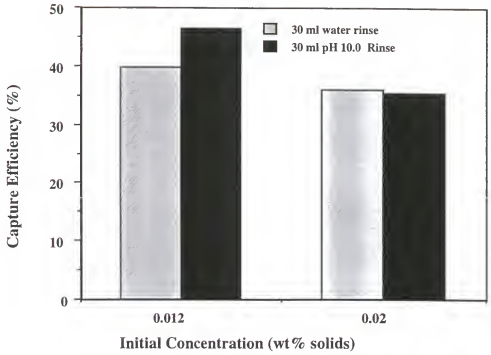


Figure 2-9. Comparison of filtration efficiency of water rinsed vs. pH 10.0 solution rinsed 10 mM DDAB treated AN06 filters for 60 nm P(S/A/V-COOH) at pH 4.0 and initial particle concentration of 0.012 wt% solids.

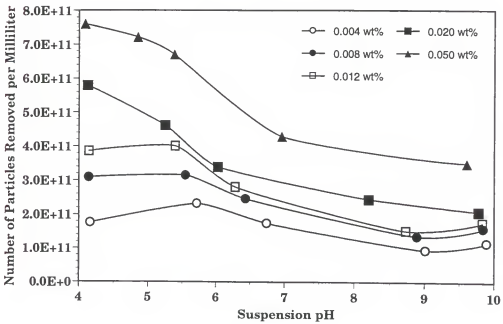


Figure 2-10. Number of particles removed per milliliter of suspension as a function of the suspension pH and initial particle concentration.

milliliter of suspension for different pH values of the suspensions. In Figure 2-11, the filtration results are plotted only for pH 4.0. It is easy to see from this graph that as the initial particle concentration increases, the number of particles removed also increases. At low concentrations, the number of particles removed increases linearly with initial particle concentration. As the initial particle concentration increases, the number of particles removed is no longer linear due to particle-particle interactions.

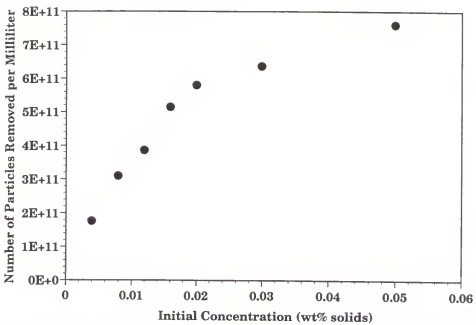


Figure 2-11. Plot of the number of particles removed per milliliter of suspension at pH 4.0 as a function of the initial particle concentration.

2.8 Effect of Ionic Strength.

As seen from the results of the filtration experiments, increasing the hydroxide concentration (increasing pH) has a detrimental effect on particle adsorption. By increasing the ionic strength, particle filtration efficiency is expect to decrease due to the

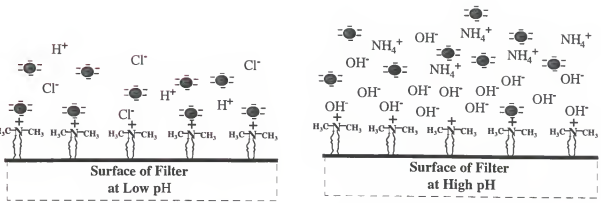


Figure 2-12. Schematic illustration of the mechanism of competitive adsorption at low and high suspension pH values.

ions interacting with the surfactant molecules on the filter surface. Salt concentrations higher than 0.10 moles/L were not used because higher concentrations would cause particle aggregation due to compression of the electrical double layer. Results for several salts are shown in Figure 2-13. Sodium chloride and potassiun sulfate have a small effect on filtration efficiency. Potassiun nitrate has the largest effect on filtration efficiency. Potassium sulfate and potassium nitrate have been shown to decrease the surface charge (zeta potential) of quaternary ammonium modified surfaces (Suhara *et al.*, 1995). None of these salts, however, has the same effect as the hydroxide ions. Hydroxide ions have a much higher affinity for surface adsorption than these salts. It has been reported that hydroxide ions have a higher surface adsorption affinity than the chloride ions on poly(etheretherketone) surfaces (Weidenhammer and Jacobasch, 1996).

2.9 Effect of Pore Diameter.

The capture efficiencies of filters with different mean pore diameters were also studied. The suspension pH of 4.0 was chosen for this study because the highest filtration efficiency is observed at this pH value, and therefore, changes will be more pronounced.

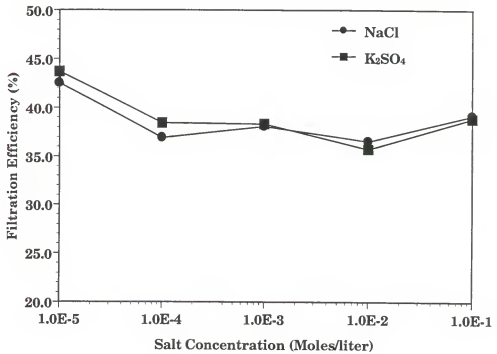


Figure 2-13. Effect of salt concentration of different salts on filtration efficiency of 60 nm P(S/A/V-COOH) particles at pH 4.0 and initial concentration of 0.012 wt% solids.

Both the untreated filters and surfactant treated filters show a sharp decrease in filtration efficiency as the pore diameter of the filters increases (Figure 2-14). However, for the 10 mM DDAB treated filters, the filtration efficiency remains much higher than the untreated filters. The decrease in filtration efficiency as pore diameter increases is expected because filtration of these nanoparticles is diffusion controlled. The electrostatic attraction between the particles and filter surface is only effective within a

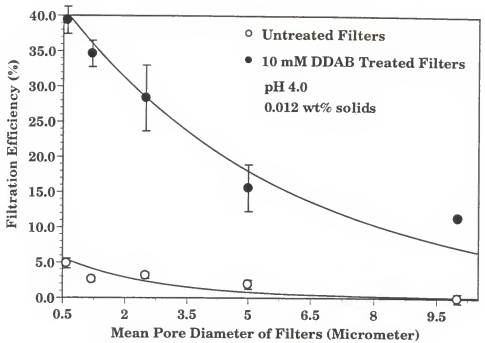


Figure 2-14. Effect of mean pore diameter on filtration efficiency of filters for 60 nm P(S/A/V-COOH) particles at pH 4.0 and initial concentration of 0.012 wt% solids.

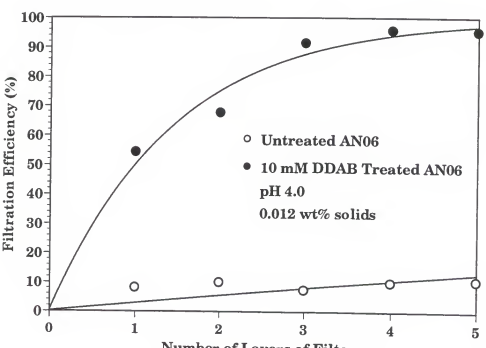


Figure 2-15. Effect of multiple layers of AN06 filters on filtration efficiency at pH 4.0 and initial particle concentration of 0.012 wt% solids.

certain distance. If the particles and surface are too far apart, each will not feel the presence of the other. When the pore sizes are too large, the particles do not have enough time to diffuse to the surface and no interaction takes place. Thus, the particles will pass straight through the filters.

2.10 Effects of Multiple Layers of Filters.

The polypropylene filters used for these experiments are very thin (150 μm). For this type of filter to be effective in any application, multiple layers of filters must be used. With just 4 thin layers of filters, more than 95% of the particles can be removed from the solution. As the number of layers of filters increases, the incremental increase in filtration efficiency levels off. In other words, by doubling the number of filters, the filtration efficiency is not doubled, and the increase with each additional filter gets smaller and smaller. In packed bed filtration (column filtration), the filtration efficiency is given by the following equation.

$$\eta = \frac{C_{in} - C_{out}}{C_{in}} = 1 - e^{-\lambda L}$$

where η is the filtration efficiency, λ is the filter coefficient, and L is the bed length or in this case, the number of filters. The treated filter data in Figure 2-15 fits this equation perfectly. Using the above equation, the filter coefficient is calculated to be 0.65/unit filter. Pressure drop is an important parameter in any filter design. The pressure drop for water is lower for the surfactant treated filters than for the untreated filters (Figure 2-16). The surfactant treatment makes the filters more wettable with water. Therefore, for the same pressure drop, more throughput can be obtained with the treated filters.

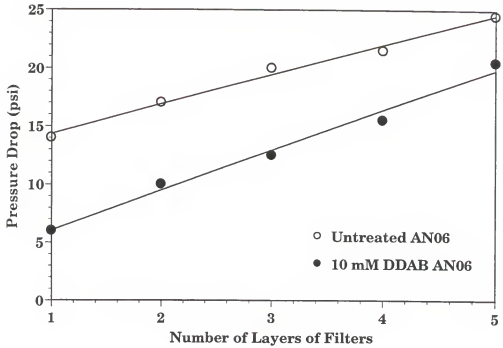


Figure 2-16. Pressure drop as a function of the number of filters for the untreated and treated AN06 filters.

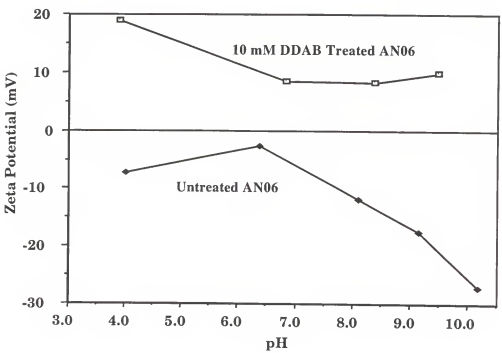


Figure 2-17. Zeta potential of untreated and 10 mM DDAB treated AN06 filters as measured by streaming potential.

2.11 Particle Adsorption Procedure

For particle adsorption experiments, the filters, both untreated and treated AN06, were rinsed with 30 ml of deionized distilled water. Each filter is then soaked in 25 ml of a particle suspension containing 0.012 wt% solids ($2.8x10^{10}$ particles/ml) of 197 nm P(S/A/V-COOH) or 200 nm P(S/Quat Ammonium) for 30 minutes. The filter is then removed from the suspension and rinsed in 100 ml of distilled water and then vacuum dried overnight before it is coated with gold for scanning electron microscopy. SEM pictures were taken with a Hitachi S4000 Field Emission Scanning Electron Microscope (Tokyo, Japan).

2.12 Particle Adsorption on Filter Surface

Since both the filters and the particles are nonconductive, they need to be coated with gold before scanning electron micrographs can be taken. Due to the limitation of the method and availability of the particles, we were confined to study adsorption of particles of larger sizes (197 nm and 200 nm) than those used in the actual filtration experiments (60 nm). The zeta potential of the untreated filters indicate that the filters are slightly negatively charged (Figure 2-17). Scanning electron micrographs of the untreated and 10 mM DDAB treated AN06 filters are shown in Figure 2-18. These filters are made by a melt-blown process and are fibrous. In the next couple of figures, the surface of the filters looks smooth because of the high magnification, focussing at small segments of individual fibers. Since the untreated filters are slightly negatively charged, it is expected that negatively charged particles will not adsorb on the surface due to the electrostatic repulsion but positively charged particles will adsorb due to the electrostatic attraction.

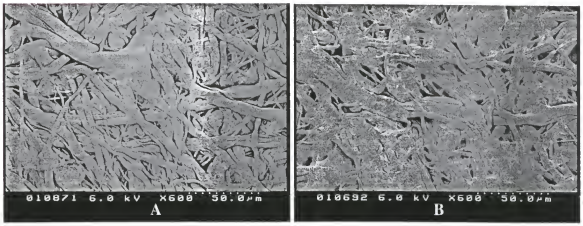


Figure 2-18. Scanning electron micrographs of (A) untreated AN06 filter and (B) 10 mM DDAB treated filter after it has been rinsed with 30 ml of deionized, distilled water.

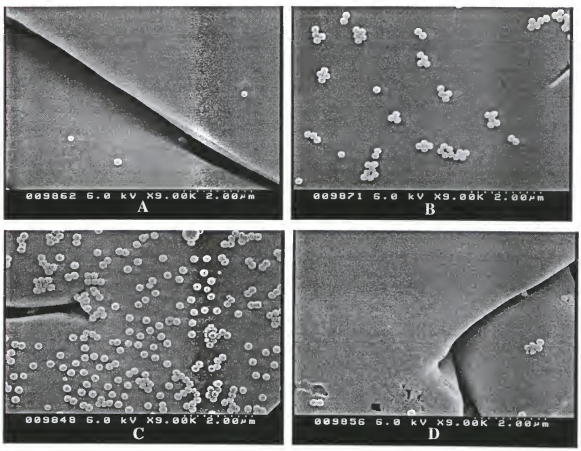


Figure 2-19. Particle adsorption on AN06 filter surfaces at pH 4.0 and 0.012 wt% solids particle concentration: (A) untreated filter and 197 nm negatively charged particles, (B) untreated filter and 200 nm positively charged particles, (C) 10 mM DDAB treated filter and negatively charged particles, and (D) 10 mM DDAB treated filter and 200 nm postively charged particles.

Experimental results are in agreement with this prediction (Figure 2-19A-B). Only a few negatively charged particles are attached to the surface of the untreated filter whereas quite a few more positively charged particles are attached. The zeta potential of the surfactant treated filters exhibit a positive charge for the whole pH range (Figure 2-17). In this case, a negligible number of the positively charged particles adsorbed on the surface. The negatively charged particles, however, are overwhelmingly attracted to the surface (Figure 2-19C-D).

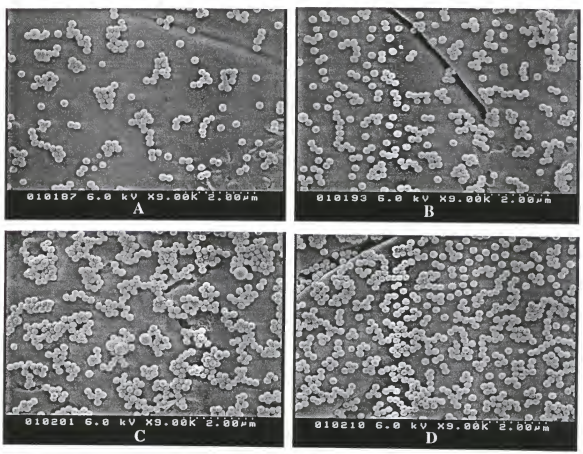


Figure 2-20. Effect of suspension concentration on the 197 nm negatively charged particle adsorption on 10 mM DDAB treated AN06 filters at pH 4.0 (A) 0.020 wt% solids, (B) 0.030 wt% solids, (C) 0.040 wt%, and (D) 0.050 wt% solids.

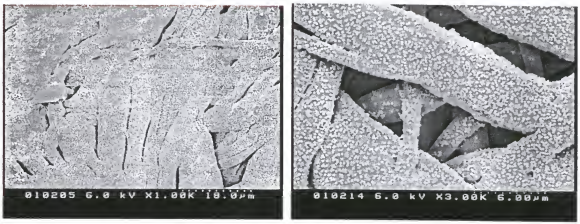


Figure 2-21. Scanning electron micrographs showing adhesion of negatively charged particles to the surface of surfactant treated filters at low magnification. The concentration of the 197 nm P(S/A/V-COOH) particles was 0.050 wt% and pH was 4.0.

Particle adsorption is also a function of the suspension concentration. By increasing the suspension concentration, more particles will diffuse to the surface of the filter and adsorb on the surface. Effects of concentrations from 0.020 wt% solids to 0.050 wt% solids are shown in Figure 2-20, which illustrates that the number of particles adsorbed on the filter surface increases with their concentration in the aqueous phase. By taking four representative pictures at each concentration, the number of particles per square micrometer can be calculated. Particle counting analysis was performed on a Macintosh computer using the public domain NIH Image program (developed at the U.S. National Institutes of Health and available on the Internet at http://rsb.info.nih.gov/nih-image/). Results along with the standard deviations between the four replicates are plotted in Figure 2-22. Although there is some scattering of the data point, there is a fairly linear correlation between the equilibrium number of particles on the filter surface and the concentration of the particles in the bulk solution. The higher the bulk concentration, the more particles adsorbed to the filter surface.

For particle adhesion to surfaces, the contact time is an important parameter. In order for the particles to stick to the surface, they must approach or collide with the surface. The number of particles adsorbed to the surface of the surfactant treated filter surface as a fucntion of contact or exposure time are shown in Figure 2-23. The particles were 197 nm negatively charged particles. The suspension concentration was 0.012 wt% and the pH was 4.0. In the first 5 minutes, the number of particles accumulating on the filter surface increased exponentially. After 5 minutes, the surface concentration of particles reached an equilibrium with the bulk concentration. These results indicate that after some usage, especially with concentrated solution, the filter will be saturated and no more particles will be removed. This process is, of course, different than

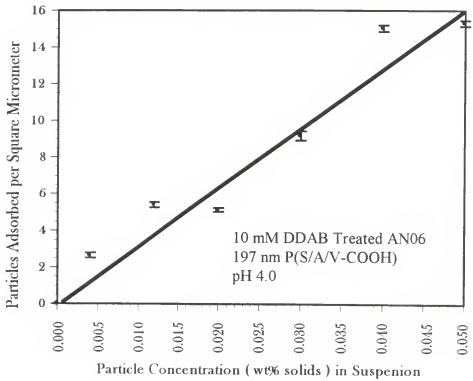


Figure 2-22. Plot of the number of negatively charged 197 nm particles per square micrometer of surface area as a function of the particle suspension concentration at pH 4.0 after 30 minutes of contact time.

conventional filtration process where the cake build up will help increase the filtration efficiency. Because the pore sizes are much larger than the size of the particles, there is very little cake build-up. The amount of particles that can be filtered with a single layer of surfactant treated AN06 filters can be estimated from the Figure 2-24. In this graph, the percent removal or filtration efficiency is plotted as a function of the volume of suspension filtered. The particle size and concentration are 60 nm (S/A/V-COOH) and 0.020 wt% solids, respectively. The high concentration was used so that saturation of the filter surface could be observed. After 90 mL of the particle concentration had been filtered, the capture efficienty of the treated filter was the same of that of the untreated filter.

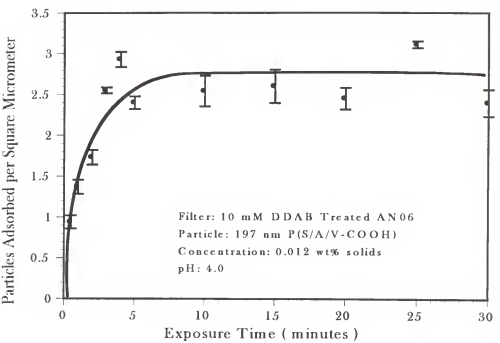


Figure 2-23. Graph of the number of particles on SEM micrograph for the 10 mM DDAB treated AN06 filter surface as a function of the soaking time or exposure time at pH 4.0 and a particle concentration of 0.012 wt%.

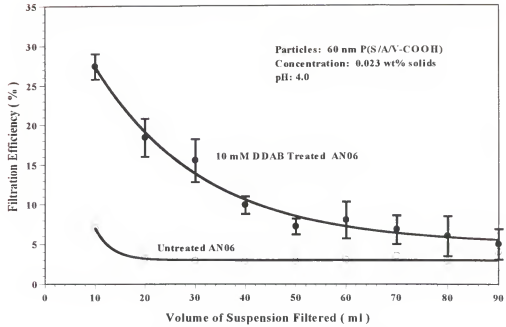


Figure 2-24. Graph showing the filtration efficiency of untreated and surfactant treated AN06 filters as a function of the volume of suspension pumped through the filters.

2.13 Summary

Due to their large pore sizes, conventional filters cannot be used to filter submicron or nanoparticles or biological particles such as bacteria or viruses. These filters must be modified to enhance the interaction between the filter and the particles. In this investigation, polypropylene membrane filters were modified with a two-tailed cationic surfactant to create a positively charged surface. Negatively charged particles can then be filtered by using electrostatic interaction between the charged particles and the polar heads of the surfactants adsorbed on the filters. Particle adsorption studies have shown that particle adsorption can be increased significantly with this treatment.

Filtration results for 60 nm negatively charged particles (carboxylate modified copolymer) filtered through DDAB treated microporous polypropylene filters show a four

to five fold increase in particle filtration efficiency. Filtration efficiency decreases as the pH of the suspension increases due to competitive adsorption between the hydroxide ions and the negatively charged nanoparticles. As the mean pore diameter increases, filtration efficiency decreases due to the increase in the distance between the particles and the oppositely charged filter surface. Multiple layers of filters can boost the filtration efficiency up to 95 percent with only 4 layers of filters. Thus, the results of this study clearly established the importance of surface modification of filters to enhance filtration efficiency by enhancing the attractive coulombic interaction between the particles and the filter surface.

CHAPTER 3
FILTRATION OF MICROBES WITH SURFACTANT TREATED POLYPROPYLENE FILTERS

3.1 Introduction

Since the surfactant treated polypropylene filters were very effective in the filtration of nanoparticles, the next logical step was to use them for filtration of bacteria and bacteriophages. Two different types of bacteria and three different types of bacteriophages were chosen for these experiments. The two bacteria were *Staphylococcus aureus* (ATCC 12600), a gram-positive bacterium, and *Escherichia coli* (ATCC 15597), a gram-negative bacterium. Bacteriophages were used as surrogates for human pathogens. Three well-studied phages were chosen to represent a wide range of properties that human pathogens may have. The phages and their respective hosts were MS2 (*Escherichia coli* C-3000), ΦX-174 (*Escherichia coli* KC), and PRD-*1 (Salmonella typhimurium*). Characteristics of these bacteriophages are listed in Table 3-1. A comparison between MS2 and PRD-1 will delineate the effect of size of viruses and that between MS2 and ΦX-174 will reveal the effect of isoelectric point or charge characteristics. All of the filtration efficiency and filter coefficient calculations are based on the number of viable bacteria and bacteriophages. Therefore, it must be pointed out that although the term "adsorption" or "adhesion" is used to account for the differences between the number of bacteria in the influent and the effluent, some of these differences

may be due to the killing of the bacteria or bacteriophages by the surface coatings or by the shearing or transport process. The filter coefficient, in essence, accounts for all mechanisms of microbial reduction in the solution. Throughout this dissertation the terms "bacteriophage", "phage", and "virus" will be used interchangeably.

3.2 Materials and Methods

The microporous polypropylene filter treatments are described in chapter 2. For the filtration of bacteria and phages, AN25 filters, which has mean pore diameter of 2.5 μm, was used in instead of the AN06 (0.6 μm) filters. By using the larger pore size filters, pressure drop was decreased and leakage through the filter holders was minimized. This was not a problem in the filtration of nanoparticles because those experiments were done with only one layer filter whereas in the microbial filtration studies, multiple layers of filters were used. The bacteria were grown overnight in a 3% tryptic soy broth and then diluted by a factor of 1000 in a buffer made of 0.02 M imidazole and 0.02 M glycine and adjusted with HCl to pH 7.0. This gives approximate initial concentrations of $2x10^5$ CFU/ml for *S. aureus* and $1x10^5$ CFU/ml for *E. coli*.

The filtration apparatus consisted of a variable speed Infusion-Withdrawal Syringe Pump (Harvard Apparatus Co., MA), six 25 mm stainless steel filter holders (Fisher Scientific) connected in series, and plastic valves and connectors for sampling ports (Figure 3-1). Each filter holder contained 1 layer of the polypropylene filter. The filters were oriented vertically and the flow direction was upward so that no air bubbles would be trapped in the filters or in the line. The flowrate was kept a constant flow of 10 ml/minute.

Table 3-1. Characteristics and Properties of Bacteriophages.

Phage	Host	Size (nm)	Structure	Type	Isoelectric
MS2	*E. coli C-3000*	24	Icosahedral	ssRNA	3.9
PRD-1	*S. typhimirium*	63	Icosahedral	dsDNA	4.2
ΦX-174	*E. coli KC*	27	Icosahedral	ssDNA	6.6

A total of 120 ml of contaminated water was pumped through the filters. After approximately 20 ml of the contaminated has passed through the filters, the first sample was taken starting from port 1 on the bottom. After all the samples from the different ports were taken, a second sample was taken from each port in the reverse order, and then a third sample was taken from each port starting from the bottom port. The samples were diluted with a solution containing 1% tryptic soy broth. Bacterial concentration was measured within 12 hours by the spread plate method (Gerhardt, 1994) using Mannitol Salt Agar for *S. aureus* and MacConkey Agar for *E. Coli*. Each sample was plated in duplicates.

The same apparatus and procedures were used in the bacteriophage filtration experiments. Initial concentrations of the phages were approximately $3x10^5$, $3x10^6$ and $6x10^4$ PFU/ml for MS2, PRD-1 and ΦX-174, respectively. The phages were assayed immediately after filtration using the soft agar overlay method described by Snudstad and Dean (1971).

In the filtration of bacteria, *S. aureus* and *E. coli* were mixed together in one solution before they were used in the experiment. Similarly, in the filtration of bacteriophages, all three phages were added to the buffer solution at one time. This was done to reduce the number of experiments required. Since both bacteria were tested at the same time, the preferential adsorption of the bacteria can also be determined from the

results. Similarly, the preferential adsorption of the phages can be observed as well. Information on the selective adsorption of one microbe over the others is important because in real life situations, the contaminated water always contains more than one type of microorganism.

3.3 Filtration of Bacteria

The zeta potentials of the untreated and surfactant treated polypropylene filters are shown in Figure 2-17. The untreated filter is negatively charged in the range of pH 4.0 to 10.0. The 10-mM DDAB treated filter, on the other hand, is positively charged in the same pH range. Results of the filtration of both *E. coli* and *S. aureus* are shown in Figure

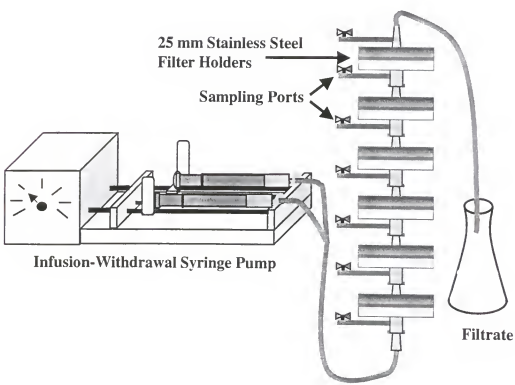


Figure 3-1. Schematic illustration of the filtration apparatus with six stainless steel filter holders, sampling ports, and a variable speed syringe pump.

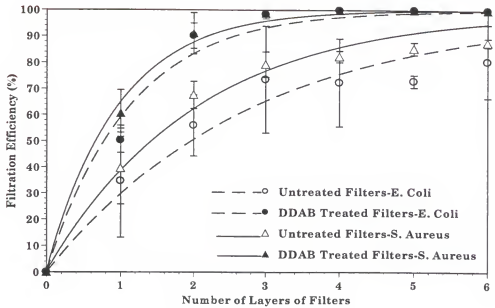


Figure 3-2. Filtration results of AN25 filters for the filtration of *E. Coli* and *S. aureus* at pH 7.

3-2. Each point on the chart is an average of six data points. The 10 mM surfactant treated filters showed much better bacterial removal than the untreated filters. The data points are fitted with the following equation in order to obtain the filter coefficient:

$$\eta = \frac{C_o - C_f}{C_o} \times 100 = (1 - e^{-\lambda L}) \times 100 \qquad (3\text{-}1)$$

where η is the filtration efficiency or percent removal, C_0 is the initial concentration in colony forming units per milliliter (CFU/ml) for bacteria and plaque forming units (PFU/ml) for phages, C_f is the final concentration, L is the length of the filter in units of number of layers, and λ is the filter coefficient with units of 1/layer of filter. Converting the results into filter coefficients is desirable for comparing the effectiveness of the different coatings for bacterial removal. The filter coefficients and coefficients of linear regression are shown in Table 3-2. The coefficient of linear regression indicates how

well the data points are fitted to the filtration equation, with a value of 1.0 being a perfect fit. The filter coefficients of the untreated filters are 0.485 and 0.353 [1/number of filters] in the filtration of *S. aureus* and *E. Coli*, respectively. The filter coefficients of the 10 mM DDAB treated filters are 1.039 and 0.896 in the filtration of *S. aureus* and *E. Coli*, respectively. From the filtration equation, it is obvious that the higher the filter coefficient, the better the filtration efficiency. The filter coefficients as defined in this work have units of 1/number of filters. In the filtration of *S. aureus*, there is a 114% improvement in the filter coefficient. In other words, to obtain the same percent removal of *S. aureus*, the untreated filters would require 114% more layers of filters than the surfactant treated filters. For the filtration of *E. coli*, the improvement in filtration coefficient is even more significant than the improvement for *S. aureus*. The improvement for *E. coli* filtration was 154%.

Table 3-2. Filter coefficient (λ) and coefficient of linear regression (R^2) for untreated and 10 mM DDAB treated AN25 for different bacteria.

	S. aureus		*E. coli*	
	λ	R^2	λ	R^2
Untreated Filter	0.485	0.984	0.353	0.958
10 mM DDAB Treated Filter	1.039	0.996	0.896	0.984
Improvement Upon Coating	114%	---	154%	---

3.4 Filtration of Bacteriophages

Filtration results for bacteriophages at pH 7 are shown in Figure 3-3, 3-4, and 3-5. Since bacteriophages are much smaller than bacteria, the filtration efficiency or percent removal of both the untreated and surfactant treated filters are not expected to be as high

as the percent removal for the bacteria. Similar to the plots for bacterial removal, each point on the graph is an average of six data points. The results for both the untreated and treated filters have a high degree of scattering or standard deviation. The data for the untreated filters have a very poor fit, R^2 of 0.28 to 0.38, when fitted to Equation 3-1. The isoelectric points (IEP), the pH at which the zeta potential is zero, of bacteriophage MS2, PRD-1 and ΦX-174 are 3.9, 4.2 and 6.6, respectively. At pH values below the isoelectric points, the phages are positively charged and at pH above the isoelectric points, they are negatively charged. Although no zeta potential as a function of pH data are available, it can be inferred from the isoelectric point that in the neutral pH range, MS2 most likely has a higher negative charge density than PRD-1 and ΦX-174. With an IEP of 6.6, ΦX-174 is only slightly negatively charged at the experimental pH of 7.0. Based on this fact, removal of ΦX-174 with the positively charged surfactant treated filters is not expected to be very efficient. The positively charged surfactant coating on the polypropylene filters greatly improved the filtration of efficiency of the filters for bacteriophages MS2 and PRD-1, but it was not effective for the removal of bacteriophage ΦX-174. The filter coefficients for the untreated polypropylene filters are 0.062, 0.069 and 0.069 for the filtration of MS2, PRD-1 and ΦX-174, respectively. As expected the filter coefficients are very low because the phages are much smaller than the bacteria. In addition, the filter coefficients for the filtration of the three different phages for the untreated filters are the same because removal is negligible and probably due to straining or entrapment mechanism.

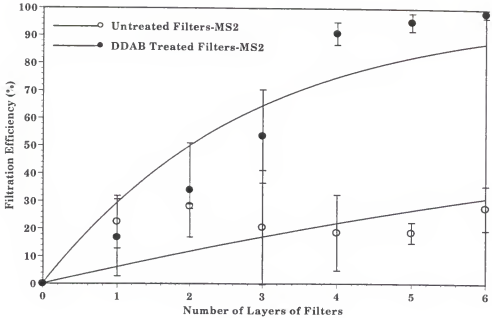


Figure 3-3. Results of phage MS2 filtration with untreated and 10 mM DDAB treated AN25 filters at pH 7.0 and flowrate of 10 ml/minute.

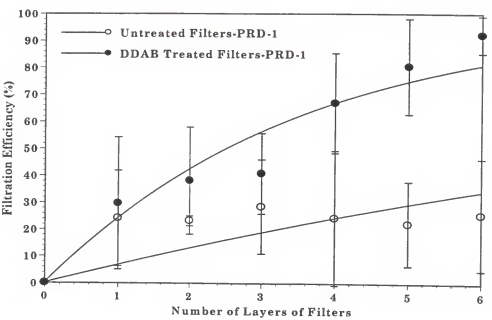


Figure 3-4. Results of phage PRD-1 filtration with untreated and 10 mM DDAB treated AN25 filters at pH 7.0 and flowrate of 10 ml/minute.

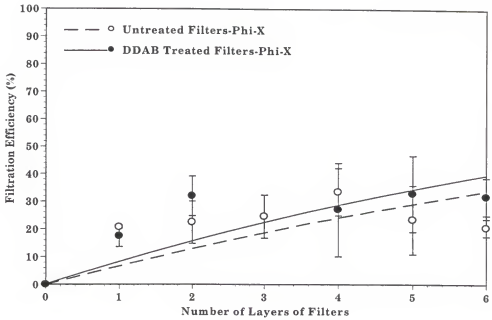


Figure 3-5. Results of phage ΦX-174 filtration with untreated and 10 mM DDAB treated AN25 filters at pH 7.0 and flowrate of 10 ml/minute.

For the surfactant treated filters, the filter coefficients are 0.345, 0.269 and 0.084 for the filtration of MS2, PRD-1 and ΦX-174, respectively. In the filtration of MS2, there is an improvement of 458% in the filter coefficient. In the filtration of PRD-1, there is an improvement of 288% in filter coefficient, but in the filtration of phage ΦX-174, only a 22% improvement is obtained. This small improvement is within the standard deviation and therefore, it can be concluded that surface modifications based on Coulombic interaction will not be helpful in the filtration of phage ΦX-174. This is possibly due to the fact that the phage is very close to its isoelectric point (i.e. pH 6.6). Bacteriophage MS2 has the lowest isoelectric point and the highest filter coefficient. These results reinforced the idea that electrostatic attraction is an important factor in bacterial and viral adsorption to surfaces.

Table 3-3. Filter coefficient and coefficient of linear regression for untreated and 10 mM DDAB treated AN25 for different bacteriophages.

	MS2		PRD-1		ΦX-174	
	λ	R^2	λ	R^2	λ	R^2
Untreated	0.062	0.279	0.069	0.357	0.069	0.374
Treated	0.345	0.920	0.269	0.913	0.084	0.602
Improvement	458%	---	288%	---	22%	---

3.5 SEM of Bacterial Adsorption

Since the concentrations used in the experiments were too low for the bacteria to be seen on the filter surface under higher magnification, the filters were soaked in a solution containing high concentrations ($1x10^7$ CFU/ml) of both *E. coli* and *S. aureus* for 30 minutes. After soaking in the solution for 30 minutes, the filters were thoroughly washed three times with deionized water. They were then placed in a container containing osmium tetraoxide vapor for two days to fix the cells so that they would not burst, rupture or shrink in the drying stage. The filters were then air-dried and coated with gold for SEM analysis. By looking at the wettability of the filters, it was apparent that the filter wettability was not uniform throughout the whole filter.

Bacterial adsorption on the filter surface was not uniform throughout the filter surface. Figure 3-6 is a low magnification scanning electron micrograph of *S. aureus* and *E. coli* adsorption on the 10 mM DDAB treated polypropylene filter. Most of the microbial adsorption occurred in the center region of the picture. Areas around the edges have some bacteria but not as high a concentration as the center region. For the untreated filter, only a few *S. aureus* and *E. coli* cells were found on the filter surface. The

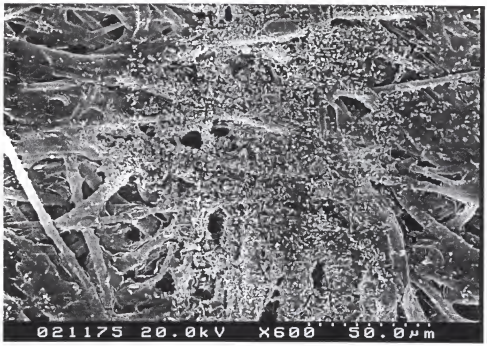


Figure 3-6. Scanning electron micrograph showing the non-uniformity of bacteria (*E. coli* and *S. aureus*) adsorption on 10 mM DDAB treated polypropylene filter.

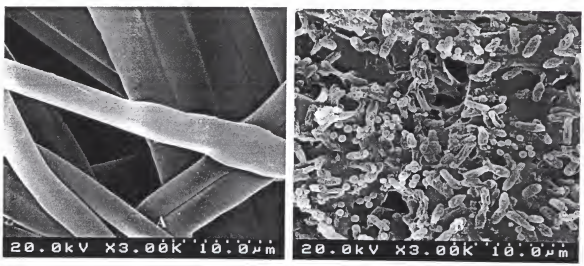


Figure 3-7. Scanning electron micrographs showing bacteria (*E. coli* and *S. aureus*) adsorption on (A) untreated and (B) 10 mM DDAB treated polypropylene filters.

surfactant treated filter, on the other hand, attracted much more bacteria to the surface of the filter, especially in localized areas as shown in Figure 3-6. Figure 3-7 illustrates

significant difference between the adsorption of bacteria on the untreated and surfactant treated filters. The spherical particles are *S. aureus* bacterium, and the rod-like particles are *E. coli* bacterium.

3.6 Summary

Microporous polypropylene filters were coated with a cationic surfactant, dimethyldioctadecylammonium bromide, to give them a positively charged surface. The zeta potentials of the unmodified as well as the modified filters were measured with a streaming potential apparatus. The surfactant treated filters were positively charged in the pH range of interest, pH 4.0 to pH 10.0. Since the bacteria are negatively charged, the filtration efficiency of the modified filters should increase compare to the unmodified filters. Results show that the filter coefficients of the surfactant treated filters has improvements of 114% in the filtration of *S. aureus* and 154% in the filtration of *E. coli*. Scanning electron micrographs confirmed that the surfactant treated filters were much more susceptible to bacterial adsorption than the untreated filters.

Three well-studied bacteriophages were used as surrogates for human pathogens. They were MS2, PRD-1 and ΦX-174. Phages MS2 and PRD-1 have similar isoelectric points, 3.9 and 4.2, but ΦX-174 has a much higher isoelectric point of 6.6. Since the experiments were performed at pH 7.0, the MS2 and PRD-1 were most likely more negatively charged than ΦX-174. Experimental results show that surface charge modification of the filters improved the filter coefficient by 458% in the filtration of MS2, 288% in the filtration of PRD-1, and 22% in the filtration of ΦX-174. These results provide conclusive evidence that surface charge modification can significantly

increase the filtration efficiency of the filters by utilizing the electrostatic attraction between the negatively charged microorganisms and the positively charged filter surface. In addition, if a virus is close to its isoelectric point (i.e. net zero charge), it will not be attracted to the filter surface irrespective of the charges on the filter surface.

CHAPTER 4
SURFACTANT TREATED MICRODENIER POLYESTER

4.1 Introduction

Polyester yarn has many consumer and industrial uses, including clothing, tire cord thread, conveying belts, waterproof canvas, and fishing nets. Microdenier polyester textile fabric was chosen for the filtration of nanoparticles and biological particles for the following reasons. In chapter 3, the effectiveness of the surfactant treated polypropylene filters was proven. The same treatment should be applicable to other types of materials. Polyester was chosen because it is readily available, and it is tenacious. Therefore, it can handle high flowrates and high pressure drops. In addition, because it is textured and woven, it increases the tortuosity of the flow path and therefore increases the probability that particles will collide with the surface of the filters. It is also chosen for the surfactant treatment so that filtration results can be compared to the results of the metal oxide coated microdenier polyester filters discussed later in this dissertation. The yarn used to make the fabric, as described in the next section, is a microdenier yarn, but the term "microdenier polyester" and "polyester" will be used interchangeably throughout this dissertation since only one type of yarn was used. Other terms, which will have the same meaning in this context are bacteriophages, phages and viruses. Bacteriophages or phages are host-specific viruses. Therefore, they will be used interchangeably.

4.2 Materials and Methods

The microdenier polyester fabric consists of a 2 x 2 right-hand twill, weighing approximately 5.5 ounces per square yard and constructed from a microdenier 1/140/200 textured polyester yarn, Type 56T Dacron® from DuPont in the warp direction and a microdenier 1/150/100 textured polyester yarn, Type 56T Dacron® from DuPont, in the filling direction. The fabric construction was 76 picks in the filling direction and 176 ends in the warp direction. Scanning electron micrographs of the untreated and surfactant treated fabric are shown in Figure 4-1 to Figure 4-4. The fabric was cut into 25-mm circles with a die cutter before the surfactant treatment was applied. Once the filters were cut into circles, they were treated with a 10 mM DDAB solution using procedures described earlier in chapter 2.

Before the filters were used in the experiments, they were flushed with 120 ml of deionized water. The filtration apparatus is described and shown in chapter 3. The sampling and filtration procedures are exactly the same as those used for the polypropylene filters with the exception that each filter holder contained four layers of these fabric filters instead of one layer.

4.3 Zeta Potential and Pressure Drop

The zeta potentials of the untreated and 10 mM DDAB treated microdenier polyester filters were measured with a streaming potential apparatus. Six layers of the fabric were used in each measurement and the results shown in the following figure are

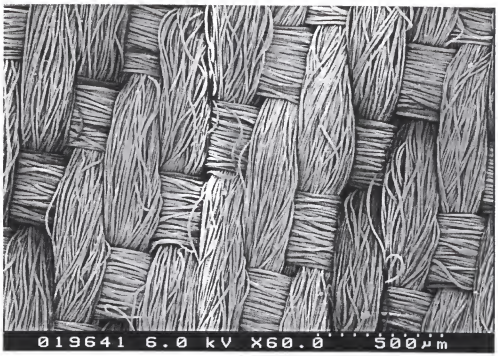


Figure 4-1. Scanning electron micrograph of untreated polyester textile fabric showing the woven pattern described in the materials and method section.

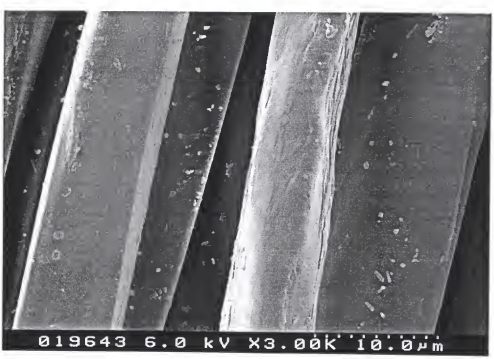


Figure 4-2. Scanning electron micrograph of untreated polyester textile fabric showing the individual fibers in the woven fabric.

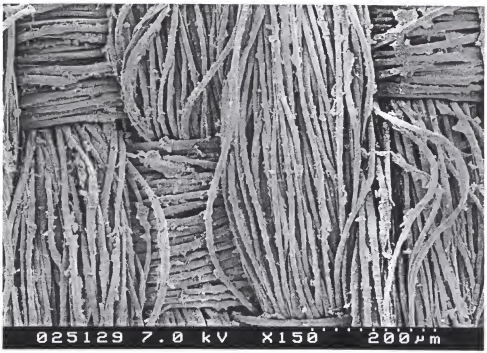


Figure 4-3. Scanning electron micrograph of 10 mM DDAB treated polyester textile fabric showing the surfactant coating on the woven patterns.

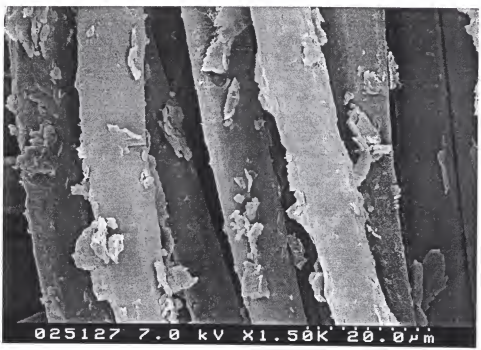


Figure 4-4. Scanning electron micrograph of 10 mM DDAB treated polyester textile fabric showing the surfactant coating on the individual fibers.

averages of three measurements. The untreated filters are negatively charged from pH 4 to pH 9.0 while the surfactant treated polyester filters are positively charged in the same pH range.

For the pressure drop experiment, the apparatus is the same as that for the filtration experiments. The flowrate was kept at a constant rate of 10 ml/minute and the pressure at each port is measures with a digital pressure gauge. From these pressures, the pressure drop for each filter holder (4 layers of fabric filters) was calculated. Each data point shown in Figure 4-6 is an average of three different measurements. For the untreated filters the standard deviations are larger than the surfactant treated filters. For the untreated filters, the pressure drops ranges from 0.7 psi for 4 layers of filters to 3.1 psi

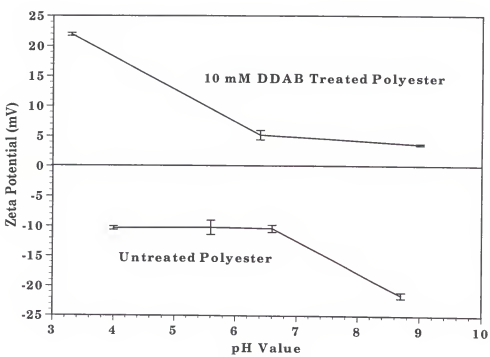


Figure 4-5. Zeta potential of 10 mM DDAB treated polyester fabric and untreated polyester fabric as measured by streaming potential.

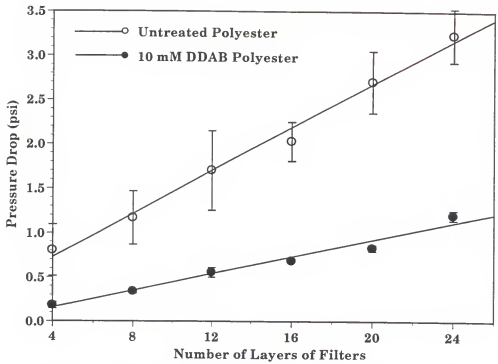


Figure 4-6. Pressure drop across the polyester fabric filters for both the untreated and 10 mM surfactant treated fabric filters along with the standard deviations for each point.

for 24 layers of filters. For the surfactant treated filters, however, the pressure drop is much lower due to the increase in wettability of the textile fabric. The pressure drops of the surfactant treated filters are 0.2 psi and 1.1 psi for 4 layers and 24 layers of the fabric filters, respectively. The decrease in pressure drop with the surfactant treatment is beneficial because it will require less energy to pass the liquid through the filters. Essentially, for the same pressure drop, more throughputs can be achieved.

4.4 Filtration of Bacteria with DDAB Treated Polyester

Two different types of bacteria were used. The gram-positive bacterium was *E. coli* and the gram-negative was *S. aureus*. These bacteria were prepared according to the procedures described in chapter 3. Filtration was done at pH 7.0 using a 0.02 M

imidazole-glycine buffer. The initial concentrations of the bacteria were approximately $1x10^5$ CFU/ml for both bacteria. Flowrate was maintained at a constant rate of 10 ml/minute with the use of a syringe pump. Samples were collected at three separate times and each sample was plated in duplicate. Therefore, each data point in the following graphs is an average of six data points. The standard deviations are also plotted. In general, the standard deviations of the untreated filters are larger than those of the surfactant treated filters. Also, the results of the first four layers always has a higher degree of scattering when compared to the rest of the filters. This is a common problem in filtration experiments, probably due to the fact that the flow has not been fully developed at the entrance of the set-up.

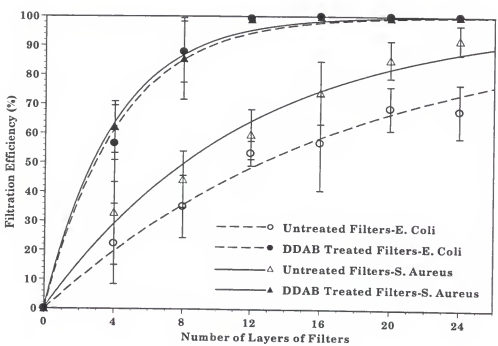


Figure 4-7. Filtration results of the polyester fabric filters for the removal of *E. coli* and *S. aureus* at pH 7.0.

Results show that the untreated polyester fabric filters removed more *S. aureus* than *E. coli*. One possible explanation is that the *E. coli* is more negatively charged than the *S. aureus* (Sonohara *et al.*, 1995), and therefore the repulsion between the filter surface and the bacterium is greater. In their study of bacterial adhesion to different fabrics, Hsieh and Merry (1986) also found that *S. aureus* has a stronger affinity for [untreated] polyester than *E. coli*. The surfactant treated polyester filter, on the other hand, removed the same percentage of both bacteria from the aqueous streams. It has been shown that for small particles (Spielman and Friedlander, 1973; Ruckenstein and Prieve, 1973; Li and Park, 1997), the process is diffusion limited once the repulsive energy barrier is removed. In this case since the surface is positively charged and the bacteria are negatively charged, there is no barrier to the adsorption or adhesion process. The rate of bacterial adsorption/adhesion to the filter surface is limited by the transport of the bacteria to the surface or the collision of the bacteria with the filter surface. Therefore, since the bacteria are of approximately the same size, it is expected that the removal would be similar for *E. coli* and *S. aureus*, which was observed experimentally.

Table 4-1. Filter coefficient and coefficient of linear regression for untreated and 10 mM DDAB treated polyester fabric filter for different bacteria.

	S. aureus		*E. coli*	
	λ	R^2	λ	R^2
Untreated Filter	0.085	0.966	0.055	0.984
10 mM DDAB Treated Filter	0.251	0.998	0.238	0.994
Improvement	195%	---	330%	---

The filter coefficients of the untreated polyester fabric filters are 0.085 and 0.055 [1/filter] for the filtration of *S. aureus* and *E. coli*, respectively. For the untreated filters, the process is not transport or diffusion limited because of the repulsive barrier between the bacteria and the filter surface. Since there is a difference in the filter coefficient or filter efficiency of the untreated filters, factors other than Coulombic interaction must be involved. It is possible that hydrophobic or other specific interactions are involved. For the DDAB treated filters, the filter coefficients are 0.251 and 0.238 for the filtration of *S. aureus* and *E. coli*, respectively. Within experimental errors, these two numbers can be considered to be identical. The surfactant treatment improved the filter coefficient by 195% for the filtration of *S. aureus* and 330% for the filtration of *E. coli*.

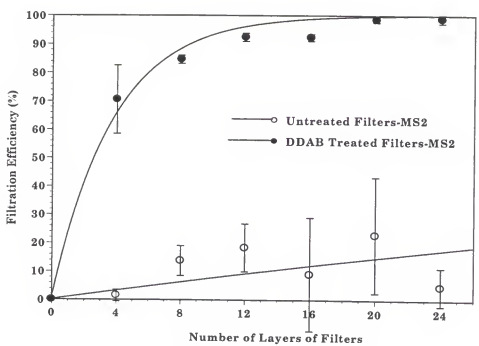


Figure 4-8. Results of phage MS2 filtration with untreated and 10 mM DDAB treated polyester fabric filters.

4.5 Filtration of Bacteriophages with DDAB Treated Polyester

The same apparatus and procedures were used in the bacteriophage filtration experiments. Initial concentration of the phages were approximately $3x10^5$, $6x10^4$ and $3x10^6$ PFU/ml for MS2, ΦX-174 and PRD-1, respectively. The phages were assayed immediately after filtration using the soft agar overlay method described by Snudstad and Dean (1971). Characteristics of the bacteriophages are listed in Table 3-1.

Results of the filtration of the different bacteriophages are shown in Figures 4-8, 4-9, and 4-10. For the filtration of MS2, only approximately 20% of the phage in the influent could be removed with 24 layers of the untreated polyester filter. These removal efficiencies are much lower than those of the bacteria because the phages are roughly 10 times smaller than the bacteria. The surfactant treatment significantly increased the

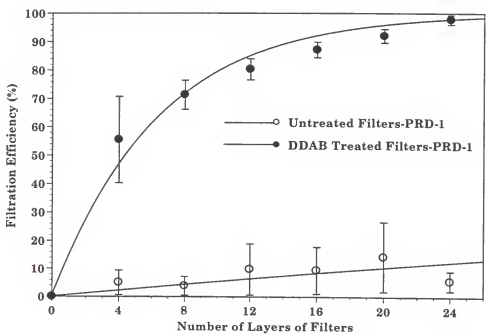


Figure 4-9. Results of phage PRD-1 filtration with untreated and 10 mM DDAB treated polyester fabric filters.

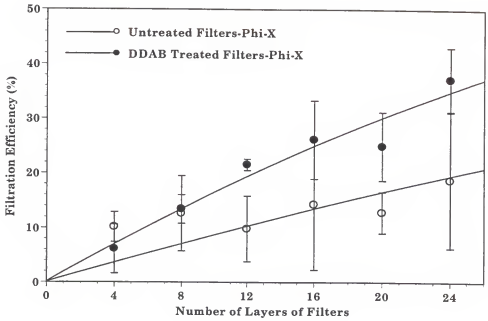


Figure 4-10. Results of phage ΦX-174 filtration with untreated and 10 mM DDAB treated polyester fabric filters at pH 7.0.

filtration efficiency of MS2. With 24 layers of the treated filters, over 98% of the MS2 in the influent were removed. Similar trends were observed for the filtration of PRD-1, with 24 layers of treated filters removing over 97% of the phage in the influent. In the filtration of bacteriophage ΦX-174, the results are very different. The surfactant treated filters were not as effective at removing ΦX-174 as they were at removing MS2 and PRD-1. Even with 24 layers of filters, less than 40% of the influent phage was removed.

All of the data points in the above figures were fitted to an exponential decay equation described in chapter 3. The filter coefficient of the untreated filters for the filtration of MS2, PRD-1 and ΦX-174 are 0.008, 0.005 and 0.009, respectively. Because of the large scattering of the data for the untreated filters, the coefficients are statistically the same. The viruses or phages are not expected to adsorb to the surface of the untreated

filters. Therefore, all of the removal is due to straining or entrapment of the particles in the structure of the filters. For the surfactant treated filters, however, the results of the different phages are very different. The filter coefficients are 0.268, 0.158 and 0.018 for the filtration of MS2, PRD-1 and ΦX-174, respectively. There is a strong correlation between the isoelectric point (IEP), the pH at which the zeta potential is zero, and the filter coefficients, and hence the filtration efficiency. The isoelectric point of bacteriophage MS2, PRD-1 and ΦX-174 are 3.9, 4.2 and 6.6, respectively. Looking at these numbers, MS2 has the lowest isoelectric point, followed by PRD-1 and then ΦX-174.

Table 4-2. Filter coefficient and coefficient of linear regression for untreated and 10 mM DDAB treated polyester fabric filter for different bacteriophages.

	MS2		PRD-1		ΦX-174	
	λ	R^2	λ	R^2	λ	R^2
Untreated	0.008	0.225	0.005	0.456	0.009	0.499
Treated	0.268	0.989	0.158	0.985	0.018	0.933
Improvement	3,270%	---	2,830%	---	98%	---

Because of the low IEP, MS2 should be the most negatively charged phage at the experiment condition, follow by PRD-1 and ΦX-174. Due to this high charge density, MS2 has the highest adsorption to the filter. The surfactant treatment increases the filter coefficient by 3300%, which means that to obtain the same percentage removal of MS2, the length (or number of filter in this case) of the untreated filters must be 33 times longer than the treated filters. The filter coefficient improves by 2800% in the filtration of phage PRD-1. In the filtration of ΦX-174, the filter coefficient improves by only 98%. This

improvement is rather insignificant because the standard deviation is fairly high. Because of its high IEP of 6.6, the phage is only slightly negatively charged at the experimental pH of 7.0. Other researchers have shown that ΦX-174 is one of the most difficult phage to remove from aqueous and air streams because of its poor adhesion to surfaces. Due to this poor adhesion to surfaces, it has been used as the particle of choice for testing barrier material such as medical gloves and condoms, where virus penetration is undesirable (Korniewicz *et al.*, 1990; Lytle *et al.*, 1991; Hamann and Nelson, 1993; Lytle and Routson, 1995).

4.6 SEM of Bacterial Adsorption

To verify that the bacteria were attracted to the surface of the filters, the first layer was examined with a scanning electron microscope after 1.0 L of the bacterial solution, containing both *S. aureus* (approximately $1x10^5$ CFU/ml) and *E. coli* (approximately $1x10^5$ CFU/ml), had passed through it. The filter was then rinsed with deionized water in a beaker to remove loose bacteria from the surface. The wet sample was prepared for SEM analysis by placing the contaminated filter in a chamber saturated with osmium tetraoxide vapor for 2 days. The filter was then taken out and allowed to dry overnight. Once the sample was dry, it was coated with a thin layer of gold. SEM analysis was done with a Hitachi S4000 Field Emission Scanning Electron Microscope (Tokyo, Japan). Pictures of the bacterial adhesion to the filter surface are shown in Figure 4-11. The four spherical particles in Figure 4-11A are *S. aureus* and the two cylindrical-shaped particles in the Figure 4-11B are *E. coli*. The amount of bacteria on the surface of the filters is very small. These pictures are not representative of the surface of the filters. There are

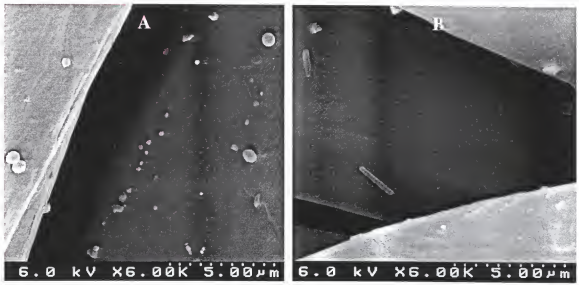


Figure 4-11. Scanning electron micrographs showing adsorption of (A) *S. aureus* and (B) *E. coli* to the surface of the surfactant treated filter during filtration.

some areas on the surface where no bacteria could be found. In the particle adsorption studies in chapter 2, the concentration of the particles are much higher, approximately $1x10^{11}$ particles/ml, but the bacterial concentration in these filtration studies are only approximately $1x10^{5}$ CFU/ml. Therefore, it is not expected that many bacteria would be found at such a small surface area, due to the magnification required to see the microorganisms. It is also possible that many of the bacteria did not survive the SEM preparation procedure. Some of the cells might have died and ruptured before they could be fixed with osmium tetraoxide vapor.

In an effort to show that the surfaces of the treated filters are truly more active than the untreated filter, solutions containing higher concentration of bacteria were used. In this study, each filter was soaked in solution containing 2.0 ml of *S. aureus* and *E. coli* mixture for 30 minutes. The bacteria solutions were taken directly from the growth broth without dilution. Their concentrations were approximately $1x10^{7}$ CFU/ml. After soaking

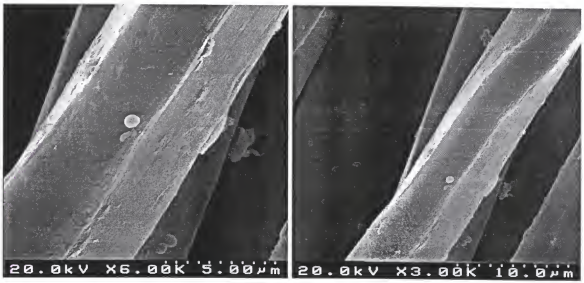


Figure 4-12. Scanning electron micrographs showing bacteria (*S. aureus* and *E. coli*) adsorption to the surface of the untreated polyester filter at different magnifications.

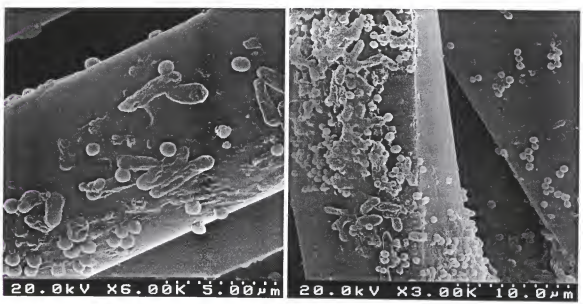


Figure 4-13. Scanning electron micrographs showing both *S. aureus* and *E. coli* adhesion to the surface of the 10 mM DDAB treated polyester filter at different magnifications and locations.

for 30 minutes, the filters were rinsed with deionized water three times before they were fixed with osmium tetraoxide vapor and analyzed according to the previous described procedure. Bacterial (*S. aureus* and *E. coli*) adhesion to the surface of the untreated

polyester fabric filter is shown in Figure 4-12. Only a few bacteria are seen in these pictures. The untreated filters are negatively charged and they will repel the bacteria rather attract them. The surfactant treated filters, on the other hand, are positively charged and the bacteria are attracted to the filter surface. As shown in Figure 4-13, there are significantly more bacteria, *S. aureus* and *E. coli*, adsorbed to the treated filter surface. These pictures provide convincing evidence that surface charge modification can substantially increase the number of bioparticles adhering to the filter surface, and hence increase the filtration efficiency.

4.7 Saturation of the Filters

To determine the capacity of the filters, two bacteria, *S. aureus* and *E. coli*, were used to challenge the filters. The initial concentrations of the bacteria were approximately $3x10^5$ CFU/ml and $1x10^5$ for *S. aureus* and *E. coli,* respectively. Both bacteria were added to the same buffer solution. The contaminated solution was pumped through two filter holders, each containing 4 layers of filters, at a rate of 10 ml/minute. Two samples were taken for analysis after 1.0 liter of solution had passed through the filters. The procedure was repeated until all of the solution had run out.

The filtration efficiency or percent removal of the filters as a function of the number of liters of solution filtered, along with its standard deviation, is shown in Figure 4-14. The results of the *E. coli* filtration with the surfactant treated filters were very scattered. After 6 liters of solution had been filtered, the surfactant treated filters were still removing more bacteria from the solution than the untreated filters. Because the untreated filters showed a decrease in filtration efficiency as more solution was passed

through the filters, it indicates that the active sites were becoming saturated or no longer available to the bacteria. Similarly, the positive sites on the surfactant treated filters were also becoming saturated with bacteria as more and more solution was pumped through the filters.

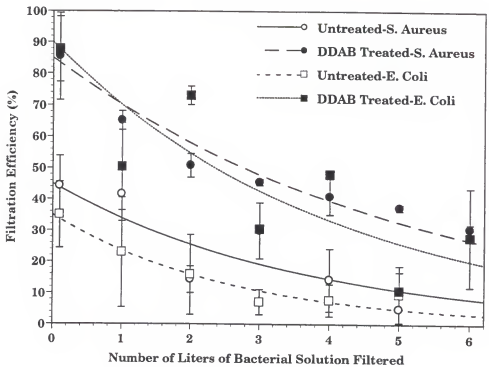


Figure 4-14. Saturation of the untreated and surfactant treated polyester filters using 8 layers of filters.

4.8 Summary

Polyester textile fabrics were coated with a water insoluble, positively charged surfactant. The hydrophobic tails of the surfactant adsorbed to the polymer backbone and the polar head was exposed to the particles in solution. The surfactant treated filters show positive zeta potential throughout the pH range of interest. The untreated fabric filters, on

the other hand, show negative zeta potential in the same pH range. Because the surfactant treatment made the fabric filters more wettable, the pressure drop across the treated filters was than that of the untreated filters.

As the particles approach the surface of surfactant treated filters, they will be attracted by the charge and be captured. The negatively charged particles, in this case, are bacteria and bacteriophages. The bacteria are *E. coli* and *S. aureus*. Three different types of bacteriophages were used. They were MS2, PRD-1 and ΦX-174. The surfactant treatment improved the filter coefficient by 195% in the filtration of *S. aureus* and 330% in the filtration of *E. coli*. In the filtration of bacteriophages, the percent improvements are much greater for the filtration of MS2 and PRD-1 than for ΦX-174. Improvements in the filtration of MS2 and PRD-1 are 3,270% and 2,830%, respectively, while the improvement for the filtration of ΦX-174 is only 98%. The differences between the improvements for the bacteriophages could be partially explained by the fact that the phages have different surface charges at pH 7.0. With an isoelectric point of 6.6, ΦX-174 is only slightly negatively charged at pH 7.0 while the other two phages have much lower isoelectric points, making them more negatively charged at the experimental condition. Therefore, the positive charge on the filter media can significantly increase the filtration efficiency of most negatively charged microorganisms.

To confirm that the bacteria are captured by the surface charge of the filter, both the untreated and surfactant treated filters were soaked in a solution containing high concentrations of both *S. aureus* and *E. coli* bacteria. Scanning electron micrographs show that the untreated filters repelled the bacteria. Only a few cells were seen on the

filter surface. The surfactant treated filters, on the other hand, has a much higher number of bacteria sticking to the surface. These results provide conclusive evidence that the increase in filtration efficiency is mainly due to the Coulombic attraction between the negatively charged bacteria (or viruses) and the positively charged surfactants on the filter surface.

CHAPTER 5
COATINGS OF IRON OXIDES ON MICRODENIER POLYESTER FABRIC

5.1 Introduction

Iron oxides are very common in the environment. As a consequence of their abundance, they are of interest to many scientific disciplines including mineralogy, geology, biology, medicine, soil science, and chemistry. There are sixteen different forms of iron oxides, and they are usually classified into three categories depending on their composition (Cornell and Schwertmann, 1996). These three categories are oxide-hydroxides, hydroxides, and oxides. The oxide-hydroxide group includes goethite, lepidocrocite, akaganeite, feroxyhyte, δ-FeOOH, and high pressure FeOOH. The hydroxide group consists of schwertmannite, ferrihydrite, bernalite, and $Fe(OH)_2$. The oxide group consists of haematite, magnetite, maghemite, β-Fe_2O_3, ε-Fe_2O_3 and wüstite. In this dissertation, they will be collectively referred to as the iron oxides. The chemical compositions of these iron oxides are listed in Figure 5-1.

In recent years, a great deal of effort has been placed on the use of metallic hydroxide flocs and metallic hydroxide coatings to remove microorganisms from contaminated water. Metallic hydroxide, including iron and aluminum, flocs have been shown to be effective for the removal of bacteria and viruses from water following settling or filtration (Bitton, 1994). They have also been used to concentrate viruses from water as a part of virus detection procedures (Vilagines *et al.*, 1982; Walter *et al.*, 1985).

Metallic hydroxide flocs were also used to coat sand and diatomaceous by using pre-formed flocs or by forming the flocs in solutions that are in contact with the media (Brown *et al.*, 1974; Edwards and Benjamin, 1989; Mills *et al.*, 1994). The treatment increases the media's ability to adsorb microorganisms from water. However, the coating procedure requires repeated treatments or long contacting times. An alternate method of coating was developed by Farrah *et al.*, in which the metallic hydroxides were formed directly on the surface of the media (Farrah and Preston, 1985; Farrah *et al.*, 1991; Lukasik *et al.*, 1996). With this method, a combination of metallic hydroxides can be deposited on the surface of the sand or other media. The combination of iron and aluminum hydroxides has been found to be more effective in removing microorganisms than the individual iron or aluminum hydroxide coating (Lukasik *et al.*, 1996). Long-term studies conducted by Ahammed and Chaudhuri (1996) showed that metal hydroxide coated sand has the potential for use in low-cost household water filters in developing countries. Surface charge interaction is hypothesized to be the primary contributor to the biofiltration process.

In all of the studies involving iron oxide/hydroxide coating, none of the researchers attempted to control the structure or form of the iron oxides. No identifications of the resulting coatings were reported. Since the coating process involves rapid precipitation of the iron oxides, it is believed that the resulting coatings composed of a mixture of different forms of the iron oxides. Therefore, the purpose of this study is to isolate the different forms of iron oxides and determine the affects each form has on bacteria and virus filtration efficiency. Three forms of the iron oxides, goethite, haematite, and magnetite, have been successfully coated on textile fabric by controlling

the pH and amount of oxygen available in the reaction. Although media other than polyester, such as other textile fabrics and sand, can be coated with the iron oxides by this method, only the results for polyester fabric will be discussed in this work.

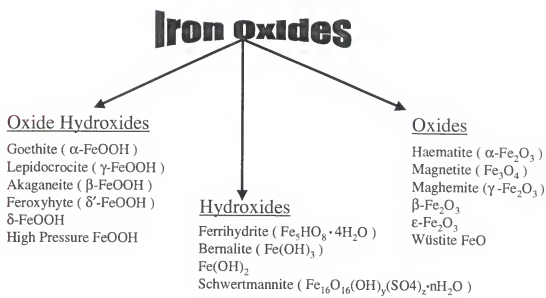


Figure 5-1. Classification of the iron oxides.

5.2 Materials and Methods

In the coating process, all reactions were carried out in a Werner Mathis dyeing machine, shown in Figure 5-2, having a rotating basket insert and a liquid capacity of approximately 3 liters. For goethite formation, the formulation consisted of 45.0 g of ferrous ammonium sulfate hexahydrate (MW=392), 3.0 g formic acid, 1.3 g ammonium formate, 1.2 g Rhodacal BX-78™, 10.0 g urea, and 2.0 L water. For the formation of haematite, the solution consisted of 15.0 g ferrous ammonium sulfate hexahydrate, 30.0 g

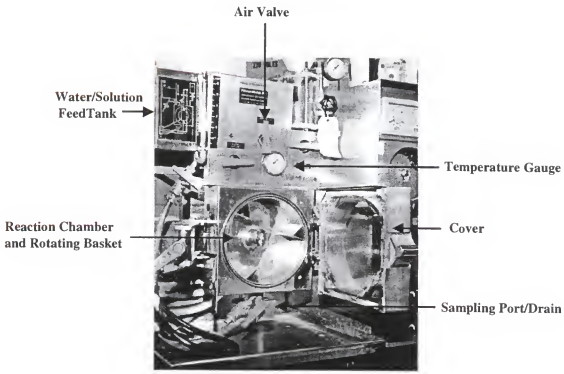


Figure 5-2. Picture of a Werner Mathis dyeing machine used in the iron and mixed oxide coating process.

urea, 1.2 g Rhodacal BX-78™ and 2.0 L water. To get magnetite coating, the solution consisted of 45.0 g ferrous ammonium sulfate hexahydrate, 60.0 g urea, 0.60 g Rhodacal BX-78™ and 2.0 L of water. Approximately 100 g of the microdenier polyester fabric was placed inside the basket of the dyeing machine. (The fabric construction is described in Chapter 4). The chemicals were mixed in a beaker and then added to the dye machine. The rate of agitation was set at approximately 60 turns per minute with an interrupted clockwise and counter-clockwise turning mode. In the goethite and haematite reactions, the air valve was closed so that the amount of oxygen in the system was limited. For the magnetite reaction, the air valve was left opened. The reaction temperature was set at 90 °C and the heating rate set at maximum. The mixture was allowed to react for two hours

after the temperature had reached the setpoint. After the two hours, the machine was set on automatic cooling and the liquor was decanted when the temperature had fallen below 50 °C. The fabric was washed three times with 2 liters of tap water, and then allowed to air dried overnight.

The filtration apparatus and procedures for the bacteria and phage filtrations are described in section 3-2. All bacteria and bacteriophage samples were prepared and assayed according to the procedures outlined in section 3-2. The only exception to the procedure is that each filter holder contained four layers of the polyester fabric rather than 1 layer due to the high permeability of the fabric. Two types of bacteria were used, *Staphylococcus aureus* (ATCC 12600) and *Escherichia coli* (ATCC 15597). The initial concentrations of the bacteria were $2x10^5$ CFU/ml for *S. aureus* and $1x10^5$ CFU/ml for *E. coli*. The bacteria concentrations were measured by the spread plate method. Three different bacteriophages were used as surrogate viruses in the filtration experiments. Initial concentrations of the phages were approximately $1x10^5$, $1x10^6$ and $1x10^5$ PFU/ml for MS2, PRD-1 and ΦX-174, respectively. Bacteriophage concentrations were measured by the soft agar overlay method.

5.3 Reaction Analysis

With the heating rate set at maximum, the content of the dye jet or reactor took 15 minutes to reach the temperature setpoint of 90 °C. After the temperature had reached 90 °C, samples were taken every half hour for pH and iron(II) depletion analysis. Iron concentration was measured by inductively coupled plasma (ICP) spectroscopy. Since the reactant, iron(II), is water soluble, the samples were allowed to settle overnight before

the solution was measured for iron content. By allowing the solution to settle overnight, the products, which were water insoluble settled to the bottom of the solution. In Figure 5-3, the rate of depletion of the reactant, Fe(II), is shown as a function of time. After the temperature has reached the setpoint, the depletion of Fe(II) is linear with respect to time, indicating that the reaction is first order. The pH of the solution was also monitored. Previous studies done at Milliken Research Corporation has shown that pH must be carefully controlled in order to obtain the desired products. Throughout the whole goethite reaction, pH remained in the vicinity of 3. For the haematite reaction, the pH was approximately 4 for the first hour. After the first hour, the pH increased due to the decomposition of the urea into NH_4OH. For the magnetite reaction, because of the high amount of urea, the pH had risen up to the 5 to 6 range only after 30 minutes at 90 °C.

The different oxides have different colors that could be used to quickly identify them. On the polyester fabric, goethite has a bright yellow color, haematite has an orange color, and magnetite has a dark brown color. The chemical reactions are believed (Cornell and Schwertmann, 1996) to be as follows:

Goethite Formation:

$$2Fe^{2+} + 3H_2O + 1/2O_2 \longrightarrow 2FeOOH + 4H^+$$

Haematite Formation:

$$2FeOOH \longrightarrow Fe_2O_3 + H_2O$$

Magnetite Formation:

$$3Fe^{2+} + 3H_2O + 1/2O_2 \longrightarrow Fe_3O_4 + 6H^+$$

In the goethite formation, the iron(II) undergoes an oxidative hydrolysis. In the haematite formation, initially, the iron formed the goethite compound and then the goethite changed to haematite. Experimentally, the color of goethite was observed in reactor in the first 45

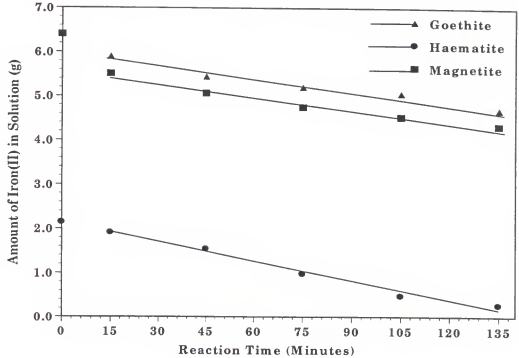


Figure 5-3. Iron(II) depletion from the reaction solution as a function of reaction time.

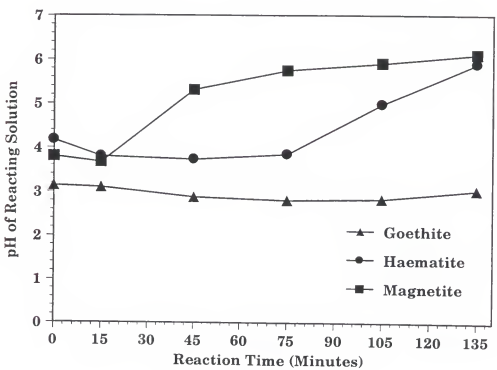


Figure 5-4. Reaction solution pH as a function of reaction time.

minutes. In the magnetite formation, the iron reacted with the abundance of oxygen to form magnetite directly. In all of these reactions, it is believed that the rate of adsorption of particles was faster than the rate of formation of particles because the solution remained clear during the treatment process. In terms of the amount of pick-up of the different coatings, the results are listed in Table 5-1. The amount of oxides per 100 g of polyester fabric was determined directly from the weight of the fabric before and after the treatment.

Table 5-1. Weight of iron oxide per 100 g of polyester fabric, measured directly from the weight of the fabric before and after the coating process.

Coating	Weight of Coating (g/100g fabric)
Goethite	2.024
Haematite	2.675
Magnetite	1.873

SEM pictures of the different coatings on the polyester fabric are shown in Figures 5-5 to 5-7. In each figure, two scanning electron micrographs are used to illustrate the difference in the amount of coating on the fibers in different orientations. The inserts in the figures show the position of the fibers in the woven fabric. In goethite coating, the fibers on the top (vertical) did not have as much coating on them as the fibers oriented in the other direction. The coating on the fibers on the top was probably removed during the washing stage. It is believed that the coatings were physically attritioned off the fibers. For the haematite coating, the coating on fibers was uniform for all the fibers regardless of the orientation since haematite had the most coating compared

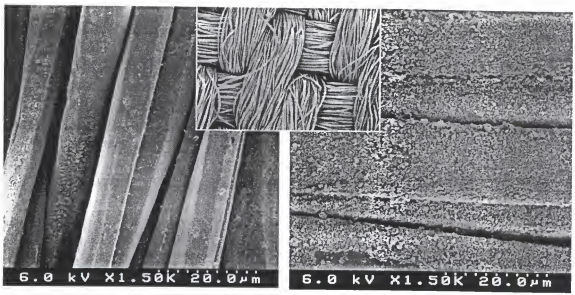


Figure 5-5. Scanning electron micrographs showing goethite coating on polyester fibers in the woven fabric shown in the insert.

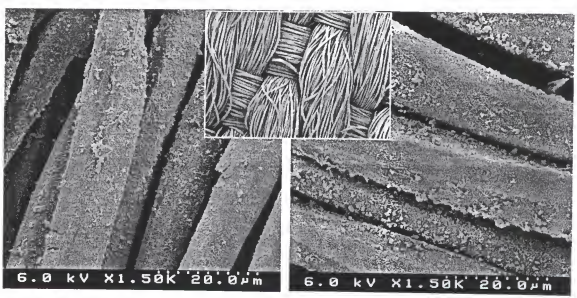


Figure 5-6. Scanning electron micrographs showing haematite coating on polyester fibers in the woven fabric shown in the insert.

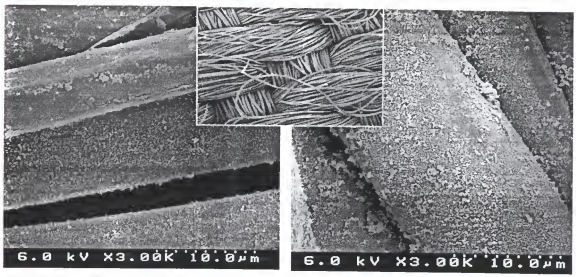


Figure 5-7. Scanning electron micrographs showing magnetite coating on polyester fibers in the woven fabric shown in the insert.

to the other two oxides. The magnetite coating showed the same result as the goethite coating. The exposed fibers did not have much coating on them as those that were protected.

5.4 Zeta Potential and Pressure Drop of the Iron Oxide Coated Polyester

Zeta potentials of the coated filters were measured with a streaming potential apparatus. All values shown in Figure 5-8 are averages of three separate measurements. The untreated polyester shows negative zeta potential for the pH range of interest. The iron oxide coated fabric filters are less negatively charged than the untreated fabric filters but they are still negatively charged in the pH range of 4 to 10. At the experimental condition, pH 7.0, the zeta potentials of goethite and magnetite coated filters were approximately -6.5 mV. At the same pH, the zeta potential of haematite coated filter was -9 mV. These values are more negative than values reported for the goethite, haematite,

and magnetite particles. The isoelectric points of all three oxide particles are reported to be in the range of 7 to 9.5 (Cornell and Schwertmann, 1996), depending on the source of the reference used. Cornell and Schwertmann (1996) also reported that isoelectric points are dependent on the ionic species in solution. These isoelectric points indicate that the iron oxide particles are positively charged at pH below 7.0. However, the zeta potential of the coated fabric filters showed that the filters were negatively charged at pH 7. This result could be explained by the fact that the polyester is negatively charged and zeta potential is a measurement of the net charge of the filter. Therefore, the positively charged coatings were offset by the negatively charged exposed polyester fibers.

The pressure drop across the filters was measured using the same set-up as the filtration apparatus. The iron oxide coated filters had significantly lower pressure drop than the untreated filters. For the untreated filters, the pressure drop ranged from 0.8 psi

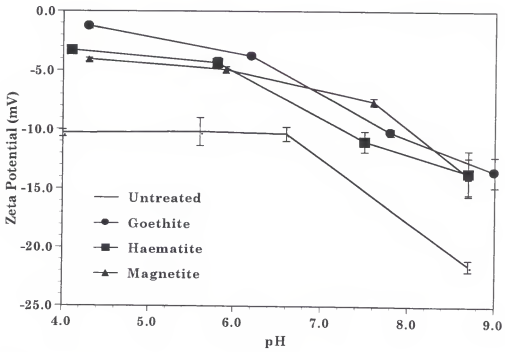


Figure 5-8. Zeta potential of untreated and iron oxide coated polyester fabric filters.

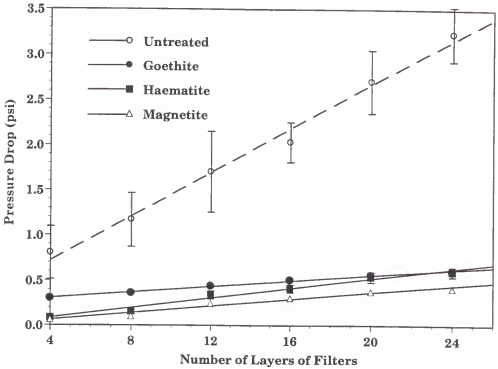


Figure 5-9. Pressure drop of untreated and iron oxide coated polyester fabric filters of a function of the number of layers of filters.

for 4 layers of filters to 3.2 psi for 24 layers of filters. The pressure drop of the iron oxide coated filters, on the other hand, ranged from 0.1 psi to 0.6 psi for 4 layers and 24 layers of filters, respectively. The lower pressure drop is highly beneficial because less energy would be required to pass the contaminated water through the filters. The decrease in pressure drop is due to the increased wettability of the coated surface. Iron oxides have been used to make non-wettable surfaces more wettable (Kenney, 1972).

5.5 Filtration of Bacteria with Iron Oxide Coated Polyester

Two different bacteria, *S. aureus* and *E. coli*, were used in the filtration experiment. Similar to previous results, each point shown in the graphs is an average of six data points. Filtration results for *S. aureus* and *E. coli* are shown in Figure 5-10 and

Figure 5-11, respectively. The standard deviations are also shown in the plots. The standard deviations of the untreated filters in both graphs are fairly large. For the iron oxide treated filters, however, the standard deviations are smaller than those of the untreated filters. In the filtration of *S. aureus*, goethite and haematite coated filters show the largest improvements. In the filtration of *E. coli*, all three oxide coatings showed similar improvements. Although the iron oxide coated filters were better at removing the bacteria from the contaminated water than the untreated filters, the improvements are not very significant when the standard deviations are taken into account.

The filter coefficients (Table 5-2) of the untreated filter are 0.085 and 0.055 in the filtration of *S. aureus* and *E. coli*, respectively. In the filtration of *S. aureus*, the filter coefficients were 0.104, 0.136 and 0.0130 for goethite, haematite and magnetite coated filters, respectively. In the filtration of *E. coli*, the filter coefficients were 0.075, 0.080 and 0.083 for goethite, haematite and magnetite coated filters, respectively. With both the untreated and iron oxide treated filters, the removal (filter coefficient) of the *S. aureus* was higher than the removal of *E. coli*. In terms of filter coefficient improvements, the results are shown in Table 5-3. The filter coefficient improvements of the oxide coated filters ranges from 22% to 60% for the filtration of *S. aureus* and 36% to 51% for the filtration of *E. coli*. Overall, the improvement is not as impressive as those of the surfactant treated filters.

The results of both the *S. aureus* and *E. coli* filtrations indicate that the process is not diffusion or transport limited because the filter coefficients of these filters were smaller than those of the surfactant treated filters. Since the filters had net negative charges, adsorption of bacteria to these surfaces are probably due to charge heterogeneity

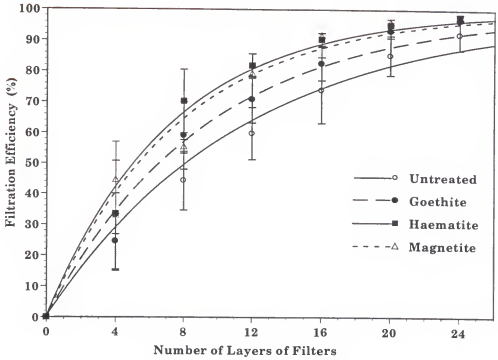


Figure 5-10. Filtration Efficiency of the untreated and iron oxide coated polyester filters for the filtration of *S. Aureus*.

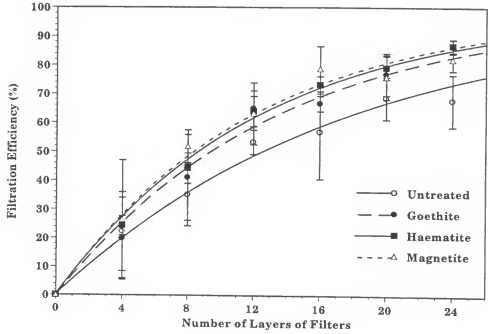


Figure 5-11. Filtration Efficiency of the untreated and iron oxide coated polyester filters for the filtration of *E. coli*.

of the surfaces. Charge heterogeneity or non-uniform distribution of charges on the surfaces of filters can greatly affect bacterial adhesion to the filters. Most surfaces in solution have charge heterogeneity at both the microscopic and macroscopic levels (Elimelech *et al.* 1995). Charge heterogeneity occurs because of surface bound impurities, crystalline structure complexities, and complex chemical compositions (Spoito, 1984; Jaroniec and Madey, 1988). Since the zeta potential of the treated or coated filters were less negatively charged than the uncoated filters, there must be areas on the surface of the filter that are positively charged so that the overall charge is only slightly negative. Surface roughness may also be responsible for the bacterial adsorption to the surface of the oxide coated filters. Surface roughness may increase adsorption of particles to surfaces by reducing the repulsive energy barrier (Elimelech and O'Melia, 1990; Verheyen *et al.*; 1993; Suresh and Waltz, 1996).

Table 5-2. Filter coefficients and coefficients of linear regression of untreated and iron oxide coated polyester filters for bacteria filtration.

Coating	*S. aureus*		*E. coli*	
	λ	R^2	λ	R^2
Untreated	0.085	0.99	0.055	0.98
Goethite	0.104	0.99	0.075	0.99
Haematite	0.136	0.99	0.080	1.00
Magnetite	0.130	0.98	0.083	0.99

5.6 Filtration of Bacteriophages with Iron Oxide Coated Polyester

Three bacteriophages were used as surrogates for human pathogens. Their characteristics, including isoelectric points, are described in Table 3-1. In the filtration of

MS2 (Figure 5-12), goethite coated filters has highest removal, follow by haematite coated filters. The magnetite coated filter has a lower removal efficiency than the untreated filters. The difference between the untreated and magnetite coated filter, however, may not be very significant because of the large scattering of the data points. It can be concluded that there was no change in filter efficiency between the two. Goethite and haematite treated filter, however, has filter coefficient improvements of 369% and 79%, respectively.

Table 5-3. Filter coefficient improvements for the iron oxide coated filters in the filtration of bacteria and bacteriophages.

Coating	*S. aureus*	*E. coli*	MS2	PRD-1	ΦX-174
Goethite	22%	36%	369%	506%	985%
Haematite	60%	45%	79%	24%	1,035%
Magnetite	53%	51%	-	65%	406%

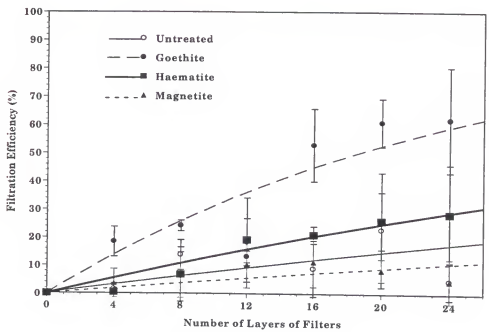


Figure 5-12. Filtration efficiency of iron oxide coated polyester filters in the filtration of bacteriophage MS2.

In the filtration of bacteriophage PRD-1 (Figure 5-13), goethite coated filters has the highest filtration efficiency or percent removal. The standard deviation of the data is also very high. The removal efficiencies of the haematite and magnetite coated filters are similar to the removal efficiency of the uncoated filters. The filter coefficients of the goethite, haematite, and magnetite coated filters are 0.033, 0.007 and 0.009, respectively. Since the filter coefficient of the untreated filters is 0.005, the filter coefficient improvements of the oxide coated filters are 506%, 24% and 65% for the goethite, haematite and magnetite coating, respectively.

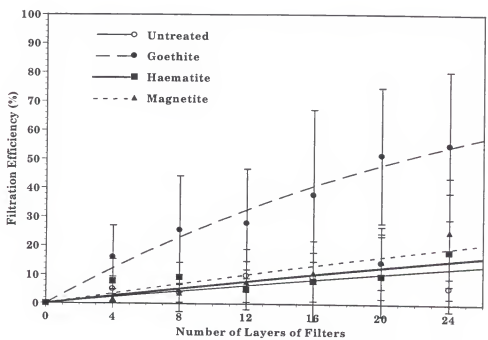


Figure 5-13. Filtration efficiency of iron oxide coated polyester filters in the filtration of bacteriophage PRD-1.

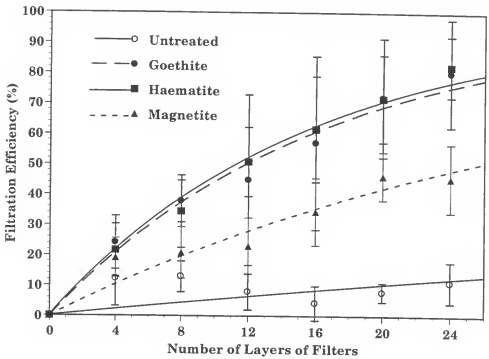


Figure 5-14. Filtration efficiency of iron oxide coated polyester filters in the filtration of bacteriophage ΦX-174.

In the filtration of bacteriophage ΦX-174, goethite and haematite coated filters show similar high removal efficiency. The removal of efficiency of the magnetite coated filters is also quite high. The filter coefficients of these three coatings are 0.059, 0.061 and 0.027 for goethite, haematite and magnetite coated filters, respectively. In terms of filter coefficient improvements, these oxide coatings has the highest percent improvements in the filtration of ΦX-174 than in the filtration of MS2 or PRD-1. The improvements for the filtration of ΦX-174 are 985%, 1,035% and 406% for coatings of goethite, haematite and magnetite, respectively.

Electrostatic interactions cannot explain the results of the bacteriophage filtration with the iron oxide coated polyester filters. With the surfactant treated filters, the results

Table 5-4. Filter coefficients and coefficients of linear regression of untreated and iron oxide coated polyester filters for bacteriophage filtration.

Coating	MS2		PRD-1		ΦX-174	
	λ	R^2	λ	R^2	λ	R^2
Untreated	0.008	0.23	0.005	0.46	0.005	0.59
Goethite	0.038	0.82	0.033	0.97	0.059	0.98
Haematite	0.014	0.94	0.007	0.63	0.061	0.99
Magnetite	0.005	0.29	0.009	0.89	0.027	0.93

are consistent with electrostatic attraction because MS2 has the highest adsorption, follow by PRD-1 and ΦX-174: MS2 has the lowest isoelectric point, follow by PRD-1 and ΦX-174. Looking at the goethite and haematite coatings, the filter coefficients are higher in the filtration of MS2 than in the filtration of PRD-1, which would be consistent with electrostatic interaction if there were positive sites on the surface of the filters due to charge heterogeneity. At a first glance, the results of the filtration of ΦX-174 seemed to be consistent with the concept of a critical surface potential. Based on this concept, if the product of the surface potential of the particle and the surface potential of the collector is below a certain value, 100 mV^2 according to Li and Park (1997), then the repulsive energy barrier is non-existent, and the adsorption process is only limited by the rate of particle diffusion to the surface. Since the isoelectric point of ΦX-174 is 6.6, the surface potential is very small around pH 7. Therefore, the product of the two potentials would be smaller than that of MS2 or PRD-1. If the results of the surfactant treated filters are taken into account, then this explanation cannot be valid. Because the surfactant treated filters are positively charged and the phage is negatively charged, the product of the two would be much smaller than the product of the phage and the iron oxide coated filters.

Following this logic, the surfactant treated filters should have a much higher filter coefficient or higher removal efficiency than the iron oxide coated filters in the filtration of ΦX-174. This is not the case. The filter coefficients of the iron oxide coated filters are much higher than that of the surfactant treated filters. These results can only lead to the conclusion that other factors or mechanisms (e.g. surface roughness, etc.) are responsible for the observed results.

The results of the filtration of ΦX-174 are puzzling but yet exciting because removal of ΦX-174 is known to be very difficult. Due to its poor adhesion to surfaces, it is the particle of choice testing barrier materials such as medical gloves (Korniewicz *et al.*, 1990; Lytle *et al.*, 1991; Hamann and Nelson, 1993; Lytle and Routson, 1995). There are applications, other than filtration, in which adsorption of these microorganisms are important such as the concentration of phages from large volumes of water. Because of the high affinity of ΦX-174 for the iron oxide coated surface, these filters may be valuable in applications where concentration of this phage is needed.

5.7 Summary

The use of metal oxides in the area of filtration has attracted the attention of many researchers in recent years. Most of the researchers used pre-formed metal oxide particles or *in-situ* precipitation of the metal oxides on the filter media. In the iron oxide treatment, most of the coating processes produced a mixture of the different forms of iron oxides. The objective of this project was to isolate several forms of iron oxides and coat them on polyester textile fabric so that they can be used for microbial removal. Three different forms of iron oxides were successfully coated on polyester fabric filters. The

oxides are goethite, haematite, and magnetite. The identities of the oxides were confirmed by visual observation of the colors and by X-ray diffraction analysis of the precipitates formed under identical reaction conditions without the fabric.

The iron oxide coated filters had zeta potentials that are less negatively charged than the untreated filters. The coatings make the filters very wettable, and therefore, the pressure drop across the filters is dramatically reduced. Low pressure is highly desirable in the filtration process because less energy would be required to pass the water through the filters.

In the filtration of bacteria, *S. aureus* and *E. coli*, the iron oxide coated filters show some improvement in filtration efficiency, as measured by the improvements in the filter coefficients. Compared to the uncoated filters, the filter coefficients of the goethite, haematite and magnetite coated filters have improvements of 22%, 60% and 53%, respectively, in the filtration of *S. aureus*. In the filtration of *E. coli*, the filter coefficient improvements are 36%, 45% and 51% for goethite, haematite and magnetite coatings, respectively.

In the filtration of bacteriophages, goethite has the highest filtration efficiency in the filtration of phages MS2 and PRD-1. Haematite and magnetite are partially effective for the filtration of MS2 and PRD-1. Phage ΦX-174, which is one of the most difficult phage to remove because of its poor adhesion to surfaces, has a very strong affinity for the iron oxide surfaces. In the filtration of ΦX-174, the improvements in filter coefficient of the oxides are 985%, 1,035% and 406% for goethite, haematite and magnetite, respectively.

CHAPTER 6
COATINGS OF IRON AND ALUMINUM OXIDE MIXTURE ON POLYESTER FABRIC FILTERS

6.1 Introduction

In the previous chapter, polyester fibers were successfully coated with three different forms of iron oxides. Although the results of the bacteriophage filtration are very promising, the results of the bacteria filtration are not as good as those of the surfactant treated filters. This is due to the fact that the iron oxide coated filters are still fairly negatively charged at neutral pH. In an effort to make the metal oxide coated filter surface more electropositive, combinations of iron and aluminum oxides were coated on polyester fabric and used to test bacteria and virus removal efficiency. Mixtures of iron and aluminum oxides, prepared by the "quick" precipitation method, on sand media have been shown to be more effective in removing bacteria than the iron or aluminum oxide individually (Lukasik *et al.*, 1996; Truedail *et al.*, 1998). The increased removal efficiency was attributed to the increase in the zeta potential of the mixed oxides. Similar to the iron oxide coatings on the sand, the oxides are most likely a combination of the different iron and aluminum oxides.

The objective of this project was to investigate the affect of the combination of goethite and aluminum oxides on the filtration efficiency in the filtration of bacteria and bacteriophages. No analysis of the resulting oxides was possible due to the amorphous structure of the mixed oxides. However, the experimental conditions were exactly the

same as those of the goethite formation reaction with the exception that the amount of ammonium iron sulfate (Mohr's salt) was changed to 15 g and aluminum sulfate was added. Therefore, it is assumed that the resulting mixture of oxides consists of goethite and aluminum oxide. No attempts were made to determine if the resulting coating is a coprecipitation of iron and aluminum oxide or if it is an aluminum substituted goethite coating. For the mixed oxides with low percentages of aluminum oxide, the treated fabric retained its yellowish color. The color turned lighter as more and more aluminum was added to the reaction because the color of aluminum oxide is white.

6.2 Materials and Methods

The mixture of iron and aluminum oxide coatings on the polyester was prepared with the apparatus and procedures as those used in the iron oxide coatings. The proportions of the different chemicals are listed in Table 6-1. For the different percentages of aluminum, the amount of iron was kept constant while the amount of aluminum was increased accordingly. All other ingredients were kept constant. In all reactions, 2.0 L of water was used.

Table 6-1. Formulations for the different ratios of the mixed iron and aluminum oxide coatings on polyester fabric.

Sample*	Mohr's Salt (g)	Aluminum Sulfate (g)	Urea (g)	Formic Acid (g)	Ammonium Formate (g)	Rhodacal BX-78™ (g)
25% Al	15.0	3.8	30.0	1.0	2.6	1.2
50% Al	15.0	12.8	30.0	1.0	2.7	1.2
75% Al	15.1	38.2	30.1	1.0	2.6	1.2
100% Al	0	15.0	30.5	1.0	2.6	1.2

* Mole percent of Al = moles of Al^{3+}/(moles of Al^{3+} + moles of Fe^{2+}) in original formulation. Molecular weight of Mohr's salt and aluminum sulfate (hydrated) are 342 and 666.42, respectively.

The filtration apparatus and procedures for the bacteria and phage filtration are described in section 3-2. All bacteria and bacteriophage samples were prepared and assayed according to the procedures outlined in section 3-2. The only exception to the procedure is that each filter holder contained four layers of the polyester fabric rather than 1 layer. The initial concentrations of the bacteria were $3x10^5$ CFU/ml for *S. aureus* and $2x10^5$ CFU/ml for *E. coli*. The bacteria concentrations were measured by the spread plate method. Three different bacteriophages were used as surrogate for human pathogens in the filtration experiments. Initial concentrations of the phages were approximately $2x10^5$, $4x10^5$ and $3x10^4$ PFU/ml for MS2, PRD-1 and ΦX-174, respectively. Bacteriophage concentrations were measured by the soft agar overlay method.

6.3 Reaction Analysis

The rates of consumption of the reactants are shown in Figure 6-1. The concentrations of the iron and aluminum were measured by ICP spectroscopy. In Figure 6-1, the solid lines are aluminum concentrations corresponding to the different mole% of aluminum in the formulation and the dash lines are iron concentrations. As the aluminum concentration increased, the amount of iron consumed in the reaction decreased. For the 25 % Al (25 mole% aluminum in the formulation), the amount of iron consumed in the reaction increased after 45 minutes, but in the other two reactions, 50% and 75% Al, the amount of iron consumed was very small.

As previously mentioned, for the goethite formation, the pH of the solution must be maintained in the acidic range. Throughout all of the reactions, the pH remained in the

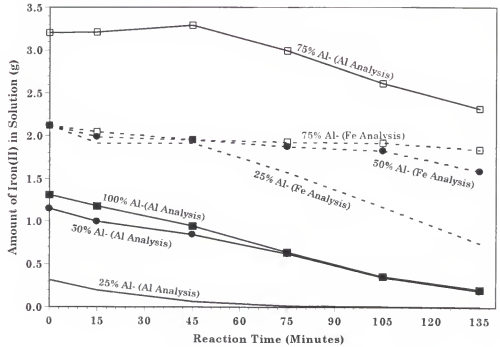

Amount of Iron(II) in Solution (g)
Reaction Time (Minutes)
75% Al- (Al Analysis)
75% Al- (Fe Analysis)
50% Al- (Fe Analysis)
25% Al- (Fe Analysis)
100% Al-(Al Analysis)
50% Al- (Al Analysis)
25% Al- (Al Analysis)

Figure 6-1. Depletion of iron(II) and aluminum from the reacting solution as a function of reaction time.

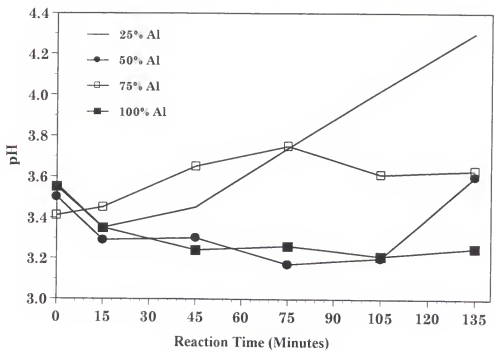


Figure 6-2. Reacting solution pH as a function of reaction time.

range of 3.1 to 4.3. The solution pH as a function of reaction time is shown in Figure 6-2. The amount of pick-up or weight of the mixed oxide coatings, as measured by weighing the fabric before and after the reaction after it was dried, is listed in Table 6-2. This method only gives a rough estimate of the amount of coating on the fabrics since the fabric as only air-dried at ambient conditions. The oxide coatings are known to absorb and retain moisture. Therefore, the weight includes the weight of the moisture. The amount of pick-up increased with the increasing amount of aluminum.

Table 6-2. Weight of mixed oxides per 100 g of polyester fabric, measured directly from the weight of the fabric before and after the coating process after the fabric had been dried.

Mohr's Salt* (g)	Aluminum Sulfate* (g)	Total Salts (g)	Percent Aluminum	Weight of Coating (g/100g fabric)
15.0	3.8	18.8	25% Al	2.95
15.0	12.8	27.8	50% Al	3.10
15.1	38.2	53.3	75% Al	4.86
0	15.0	15.0	100% Al	1.76

*Amount of Mohr's salt (ammonium iron sulfate) and aluminum sulfate in formulation.

Scanning electron micrographs of the mixed oxide coatings are shown in Figures 6-3 to 6-6. The coating on the 25% Al mixture looks the same as the goethite coating. On some of the fibers of the 50% Al mixture, the coatings are very smooth due to the aluminum oxide. Similar result was observed for the 100% aluminum oxide coated polyester. The coating is coherent and uniform. The 75% Al mixed oxides has a very different structure than those of the other mixtures. The coating on the 75% Al mixed oxides comprises of discrete colloidal particles (Figure 6-5).

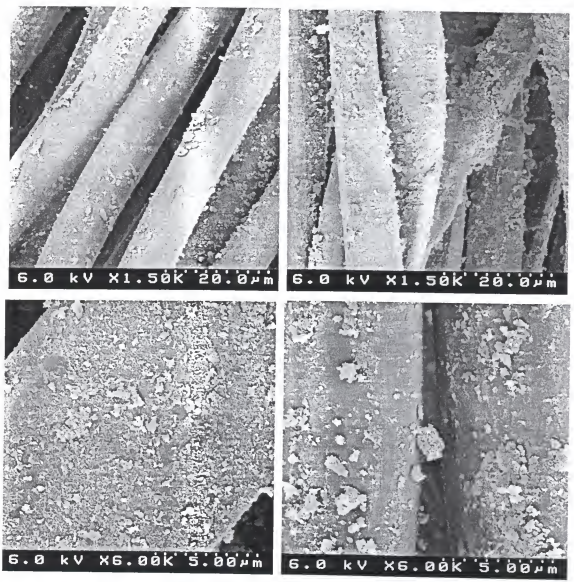


Figure 6-3. SEM of 25% Al mixed oxide coating on polyester fibers.

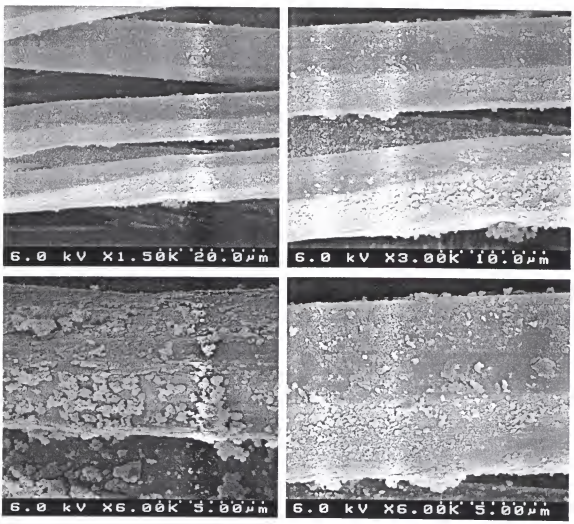


Figure 6-4. SEM of 50% Al mixed oxide coating on polyester fibers.

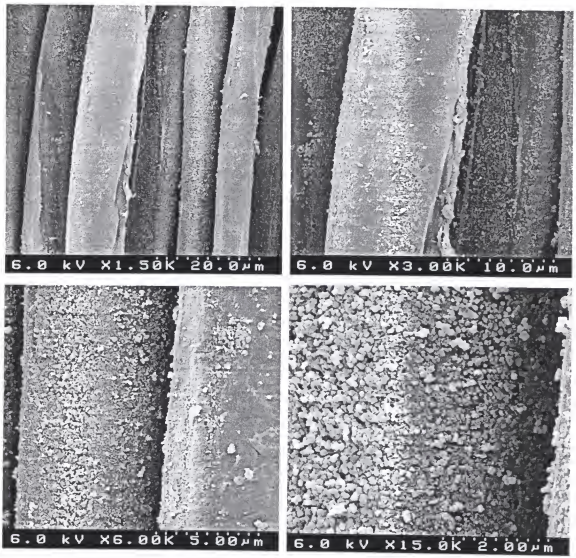


Figure 6-5. SEM of 75% Al mixed oxide coating on polyester fibers.

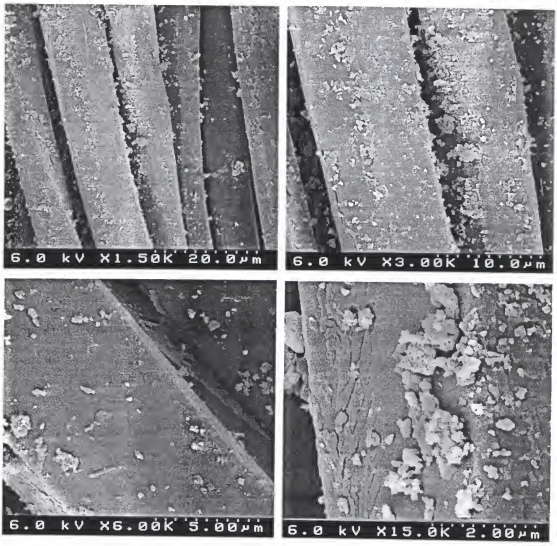


Figure 6-6. SEM of 100% Aluminum oxide coating on polyester fibers.

6.4 Zeta Potential of the Mixed Oxide Coated Polyester Filters

The zeta potentials of the mixed oxide treated polyester filters were measured three times. The average values, along with the standard deviations, are shown in Figure 6-7. The zeta potentials of the iron oxide coated filters were all negative in the pH range of 4.0 to 10. The goethite coated filters will be referred to as "100% Fe" coated filters. Unlike the iron oxide coated polyester filters, these mixed oxide coated filters exhibit positive zeta potentials in the acidic pH range. All of the isoelectric points are between 6 and 7. Since the experiments were performed at pH 7, the charge of the filters at this pH is very important. At pH 7, the aluminum oxide (100% Al) treated filter show a slight net negative charge. Compared with all the other mixtures of oxides, the 75% Al sample is the most electronegative. These results are promising because the mixed oxide treated

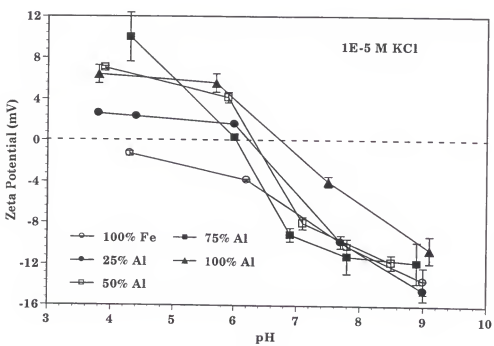


Figure 6-7. Zeta potential of mixed oxides of iron and aluminum on polyester filters.

filters are more electropositive or less electronegative than the iron oxide coated filters. Therefore, favorable electrostatic interactions between the microorganisms and the filters should be increased.

6.5 Filtration of Bacteria with Mixed Oxide Coated Polyester Fabric Filters

The same two bacteria, *S. aureus* and *E. coli*, were used in the filtration experiments with mixed oxide coated filters. In all of the graphs, the goethite coated filters are referred to as "100% Fe" for comparison purposes. The different percentages of aluminum are moles of aluminum metal to total metal (moles of iron + moles of aluminum) in the formulation. It does not necessarily indicate the percentage of aluminum oxide to iron oxide on the filter surface. In the filtration of *S. aureus*, the 75% Al is more effective than iron oxide coated filters but not as effective as the 25% Al, 50% Al, or the 100% Al coated filters. The latter three have very similar filtration efficiencies. The filter coefficients and the coefficients of linear regression are listed in Table 6-3. The filter coefficients of the 25% Al, 50% Al, 75% Al and 100% Al coated filters are 0.195, 0.180, 0.139 and 0.179, respectively, in the filtration of *S. aureus*. In terms of filter coefficient improvements over the untreated filters, the improvements are 130%, 112%, 63% and 111% for 25% Al, 50% Al, 75% Al and 100% Al coated filters, respectively.

In the filtration of *E. coli*, the 75% Al coated filter, once again, has the worst filtration efficiency compared to the other mixtures of oxides. The 25% Al, 50% Al and 100% Al coated filters have very similar removal efficiency. The filter coefficients of the 25% Al, 50% Al, 75% Al and 100% Al coated filters are 0.148, 0.154, 0.094 and 0.156, respectively. All of the filter coefficients in the filtration of *E. coli* are lower than the

filter coefficients of the same filters in the filtration of *S. aureus*, indicating that *E. coli* is somewhat more difficult to remove due to the fact that it is more negatively charged than *S. aureus*.

The fact that the 75% Al coated filters performed poorly in both bacteria filtration tests was consistent with the expected electrostatic interaction. Zeta potential measurements indicate that the 75% Al mixed oxide coated filter is the most electronegative at pH 7. Therefore, bacterial adhesion is not expected to be higher than the other mixed coatings. The structure of the coatings seems to indicate that the coatings are different than those of the other mixtures. All of the other mixed coatings have fairly smooth, coherent coatings, where as the 75% Al has patches of coatings. Similar to the iron oxides, there are many forms of aluminum oxides. Because of the large difference in the bacterial removal properties, more work needs to be done to determine the different forms of aluminum oxides on the filter surface.

Table 6-3. Filter coefficients and coefficients of linear regression of untreated and mixed oxide coated polyester filters for bacteria filtration.

Coating	*S. aureus*		*E. coli*	
	λ	R^2	λ	R^2
Untreated	0.085	0.99	0.055	0.98
100% Fe	0.106	0.99	0.074	0.99
25% Al	0.195	1.00	0.148	0.98
50% Al	0.180	0.99	0.154	0.99
75% Al	0.139	1.00	0.094	0.97
100% Al	0.179	0.98	0.156	0.96

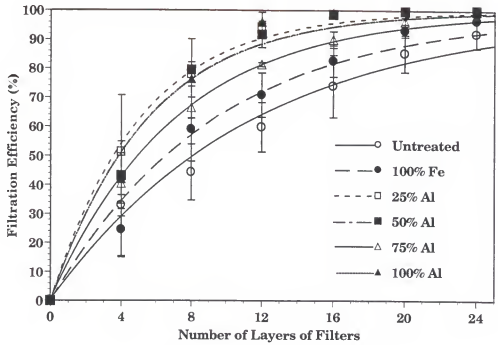


Figure 6-8. Filtration Efficiency of the uncoated and mixed oxide coated polyester filters in the filtration of *S. Aureus*.

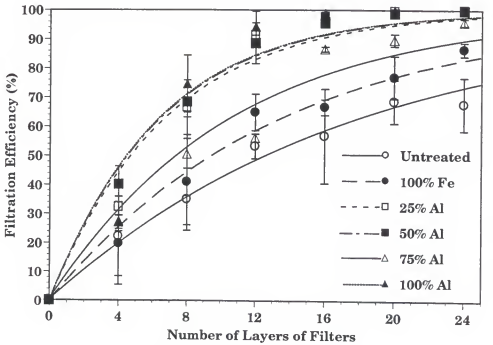


Figure 6-9. Filtration Efficiency of the uncoated and mixed oxide coated polyester filters in the filtration of *E. coli*.

Table 6-4. Filter coefficient improvements for the mixed oxide coated filters in the filtration of bacteria and bacteriophages.

Coating	*S. aureus*	*E. coli*	MS2	PRD-1	ΦX-174
100% Fe	22%	36%	564%	506%	985%
25% Al	130%	169%	1,595%	1,719%	2,130%
50% Al	112%	180%	1,956%	1,863%	1,823%
75% Al	63%	70%	704%	596%	1,029%
100% Al	111%	183%	2,083%	1,761%	2,280%

6.6 Filtration of Bacteriophages with Mixed Oxide Coated Polyester Fabric Filters

Results of the filtration of bacteriophages are shown in Figures 6-10 to 6-12. Although the results for goethite, 100% Fe, are plotted for comparison, their standard deviations are not shown in the graphs. The standard deviations of the goethite treated filters are shown in chapter 5. Similar to the filtration of bacteria, the 75% Al oxide coated filters has the worst efficiency in all phage filtrations compared to the other ratios of mixed oxides. In the filtration of phage MS2, the 100% Al coated filters has the highest removal. The 50% Al coated filters has the second highest removal efficiency, followed by the 25% Al and the 75% Al coated filters. The change in the filter coefficients are 1,595%, 1,956% and 2,083% for the 25% Al, 50% Al and 100% Al coated filters, respectively, in the filtration of MS2. For the same phage, the 75% Al coated filters only has an improvement of 704%.

Results for the filtration of phage PRD-1 are very similar to those of phage MS2. The improvements in filter coefficients range from 1,700% to 1,900% for the 25% Al, 50% Al and 100% Al coated filters. The filter coefficient of the 75% Al coated filters

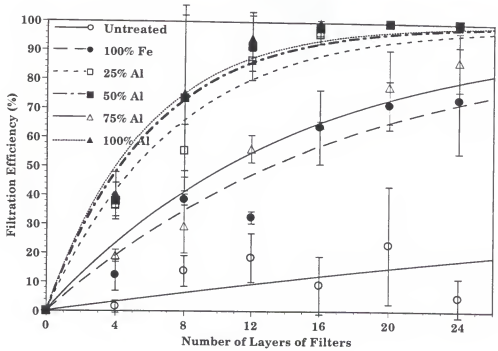


Figure 6-10. Filtration Efficiency of the uncoated and mixed oxide coated polyester filters in the filtration of bacteriophage MS2.

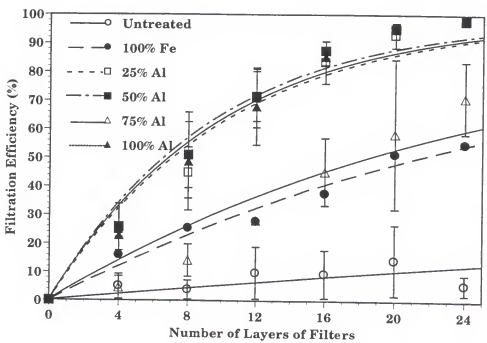


Figure 6-11. Filtration Efficiency of the uncoated and mixed oxide coated polyester filters in the filtration of bacteriophage PRD-1.

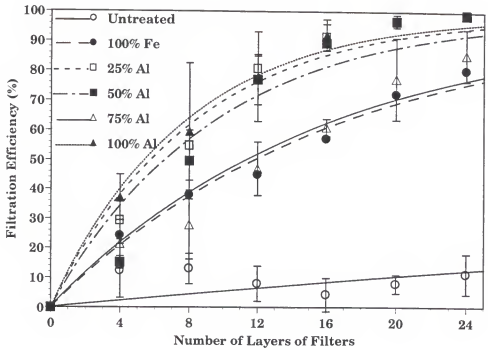


Figure 6-12. Filtration Efficiency of the uncoated and mixed oxide coated polyester filters in the filtration of bacteriophage ΦX-174.

Table 6-5. Filter coefficients and coefficients of linear regression of untreated and mixed oxide coated polyester filters for bacteriophage filtration.

Coating	MS2		PRD-1		ΦX-174	
	λ	R^2	λ	R^2	λ	R^2
Untreated	0.008	0.23	0.005	0.46	0.005	0.59
100% Fe	0.038	0.82	0.033	0.97	0.059	0.98
25% Al	0.135	0.97	0.098	0.98	0.120	0.98
50% Al	0.163	0.98	0.106	0.98	0.104	0.96
75% Al	0.064	0.97	0.038	0.93	0.061	0.96
100% Al	0.174	0.98	0.100	0.98	0.128	0.99

improves by only 596%. In the filtration of phage ΦX-174, the results were, once again, very surprising. As previously mentioned in chapter 4 and 5, bacteriophage ΦX-174 is

one of the most difficult phage to remove from aqueous streams due to its poor adhesion to surfaces. With the mixed oxide coatings, the removal efficiencies are surprisingly high. The filter coefficients are 0.120, 0.104, 0.061 and 0.128 for the 25% Al, 50% Al, 75% Al and 100% Al coated filters, respectively. With these filter coefficient, the percent improvements over the untreated filter are 2,130%, 1,823%, 1,029% and 2,280% for the 25% Al, 50% Al, 75% Al and 100% Al coated filters, respectively.

6.7 Summary

Mixed oxides of iron and aluminum were coated on polyester fabric filters. Different ratio of aluminum and iron were used in the formulation. The four different mixed oxide coated filters has 25, 50, 75, and 100 mole% of aluminum in the formulation. Reactions were carried out under those conditions which would produce goethite coating with the iron oxides. Therefore, it is assumed that the resulting mixed oxides composed of goethite and aluminum oxide/oxides. The coated filters show positive zeta potentials in acidic pH and changes to negative as the pH increases. All of the isoelectric points of the mixed oxide coated filters are between 6 and 7. Out of the mixed oxide coated filters, the 75% Al sample is the most electronegative at the experimental pH of 7.0.

In the filtration of *S. aureus* and *E. coli*, the mixed oxides are better than the iron oxides. Out of the mixed oxide coated filters, the 75% Al coated filters has the poorest performance. The 25% Al, 50% Al and 100% Al oxide coated filters have very similar filtration efficiencies for both bacteria. With the exception of the 75% Al coated filters, the mixed oxide coated filters have filter coefficient improvements of 111% to 130% in

the filtration of *S. aureus* and 169% to 183% in the filtration of *E. coli*. The 75% Al mixed oxide coated filter has improvements of only 63% in the filtration of *S. aureus* and 70% in the filtration of *E. coli*.

In the filtration of bacteriophages, the mixed oxides also performed much better than the iron oxide coatings. Similar to the filtration of bacteria, the 25% Al, 50% Al and 100% Al coated filters have identical filtration efficiencies. The 75% Al coated filters has the worst performance out the mixed oxide coated filters. In the filtration of MS2, the improvements range from 1,600% to 2,100% for the 25% Al, 50% Al and 100% Al coated filters. In the filtration of PRD-1, the improvements for the same three filters ranged from 1,700% to 1,900%. Finally, the same three filters had slightly better improvements of 1,800% to 2,300% in the filtration of ΦX-174.

CHAPTER 7
UNCONTROLLED PRECIPITATION OF THE MIXED IRON OXIDES ON POLYESTER FABRIC FILTERS

7.1 Introduction

Precipitation of metal hydroxides on both sand and fibrous media has been studied by many researchers (see Chapter 5). In Chapter 5, the reaction for producing goethite, haematite and magnetite was precisely controlled. However, many researchers have produced iron oxides precipitated by mixing iron salt solution with a strong base. In such cases, the precipitate is amorphous and presumably consists of mixtures of various forms of iron oxides. In this chapter, the *in-situ* precipitation method was used to coat iron oxides on the polyester fabric filters. As previously discussed, there are several drawbacks to the "quick" precipitation or *in-situ* precipitation method, including clogging of the pores. This was done, however, to compare the effectiveness of such coating with those of the goethite, haematite and magnetite coatings. The identity of the *in-situ* precipitated iron oxide or oxides is not known because x-ray diffraction analysis could not be performed due to the amorphous structure of the precipitate.

7.2 Materials and Methods

Several different procedures for treating the polyester fabric were tried. The best procedure was to soak the polyester filters in $FeCl_3$, dried the filters overnight, and then precipitate the iron oxides with a strong ammonium hydroxide solution. The filters were

then dried overnight in a vacuum oven. The optimum $FeCl_3$ concentration was determined to be 0.4 M. The concentration of NH_4OH used was 2 M. These concentrations were chosen so that the maximum amount of coating could be deposited on the filter surface without clogging the filters. The selection of the above concentration was also based on visual observation of the uniformity of the treated filters. The filters treated with the 0.4 M $FeCl_3$ was the most uniform compared to the others. Figure 7-1 shows the affect of different concentration of $FeCl_3$ on the coatings on the filter surface.

Filtration was performed using the apparatus and procedures described in Section 3.2. The only exception was that each filter holder had four layers of the filters instead of one layer due to the high permeability of the fabric filters. The initial concentrations of *S. aureus* and *E. coli* were approximately $2x10^5$ and $1x10^5$ CFU/ml, respectively. Initial concentrations of the bacteriophages were $1x10^5$, $1x10^6$ and $1x10^4$ PFU/ml for MS2, PRD-1 and ΦX-174, respectively.

7.3 Zeta Potential and Pressure Drop of the Filters

The zeta potential of the iron oxide coated filters, along with the standard deviation of the measurements, is shown in Figure 7-2. The zeta potential of the precipitated iron oxide coated filters is positive below pH 4. The isoelectric point of the treated filters is approximately 4.5. At the experimental pH, the treated filters are slightly less electronegative than the untreated filters. The treated filters were more wettable than the untreated filters. The pressure drop of the untreated filters was 0.8 psi across 4 layers of filters and 3.3 psi across 24 layers of filters. The pressure drop of the iron oxide treated filters, on the other hand, was only 0.1 psi across 4 layers of filters and 1.2 psi

across 24 layers of filters. The pressure drop of the treated filters was significantly lower than the untreated filters.

7.4 Filtration of Microbes with Uncontrolled Precipitated Iron Oxide Coated Polyester Fabric Filters

Results of the filtration of bacteria show that the precipitated oxide coating is not as effective as the oxides prepared by other methods. Results of the filtration of *S. aureus* and *E. coli* are shown in Figure 7-4. The filter coefficient of the iron oxide coated filters

Figure 7-1. Affect of FeCl3 treatment concentration on the formation of iron oxides on the filter surface.

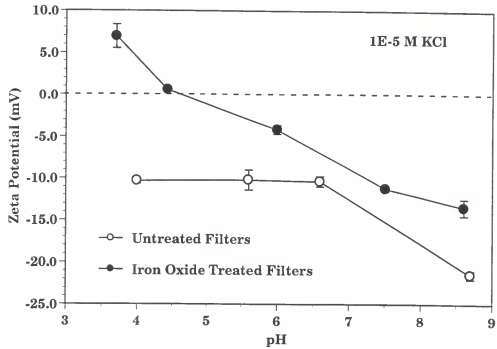


Figure 7-2. Zeta potential of untreated and precipitated iron oxide coated polyester filters.

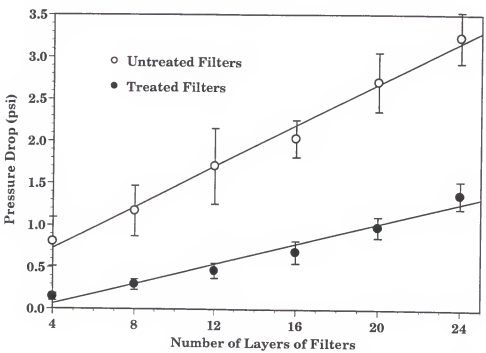


Figure 7-3. Pressure drop of untreated and precipitated iron oxide coated polyester filters.

improves by only 18%, from 0.085 to 0.100, in the filtration of *S. aureus*. In the filtration of *E. coli*, the treated filters show no improvement at all.

The treated filters have better performance in the filtration of bacteriophages. Results of the bacteriophage filtrations are shown in Figures 7-5 to 7-7. In the filtration of MS2, the filtration efficiency of the precipitated iron oxide coated filters is significantly higher than that of the untreated filters. The treatment or coating improved the filter coefficient by 500%. In the filtration of PRD-1, the coating increased the filter coefficient by 516%. In the filtration of ΦX-174, the filter coefficient is even higher. The filter coefficient of the treated filters in the filtration of ΦX-174 is 0.08, which is an improvement over the untreated filters of 1,388%.

The zeta potential of the precipitated oxide treated filters is very similar to those of the goethite, haematite, and magnetite coated filters. A comparison between the controlled coating of goethite and the uncontrolled precipitation of iron oxide coating is given in Table 7-3. In terms of microbial removal efficiency, the results are similar to those of the goethite coated filters, but slightly better in the removal of the phages. These results seem to indicate that the precipitated iron oxides composed of mainly goethite. Since the effectiveness of the precipitated oxide or oxides have better removal of phages than the three pure iron oxides, there is a possibility that other forms of iron oxides may be more effective at removing microorganisms from aqueous streams.

These results also provide evidence that the removal of the microoganisms is, in fact, due to the increased interaction between the microoganisms and the filter surface. If straining or entrapment were the primary mechanism, then the removal of the larger particles, mainly bacteria, would be higher than the removal of phages since the bacteria

are at least 10 times larger than the phages. In this case, the removal of bacteria is insignificant compare to the removal of the bacteriophages. With this increased in favorable interaction, the filtration efficiency of the phages is higher than the filtration efficiency of the bacteria because the phages have higher mobility or diffusion coefficient than the bacteria due to its smaller size. The increased Brownian motion, most likely,

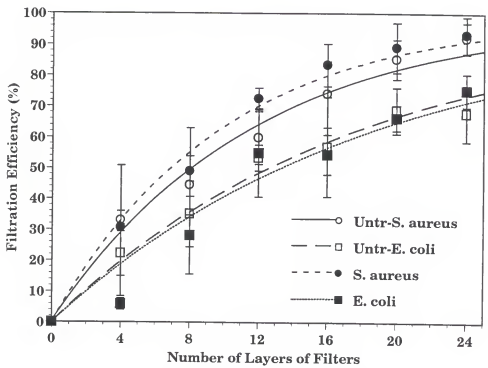


Figure 7-4. Filtration Efficiency of the uncoated and precipitated oxide coated polyester filters in the filtration of *S. aureus* and *E. coli*.

Table 7-1. Filter coefficients, coefficients of linear regression, and filter coefficient improvements of the precipitated iron oxide coated polyester filters in the filtration of *S. aureus* and *E. coli*.

	S. aureus		*E. coli*	
	λ	R^2	λ	R^2
Untreated Filters	0.085	0.99	0.055	0.98
Treated Filters	0.100	0.99	0.052	0.96
Improvement	18%	--	-5%	--

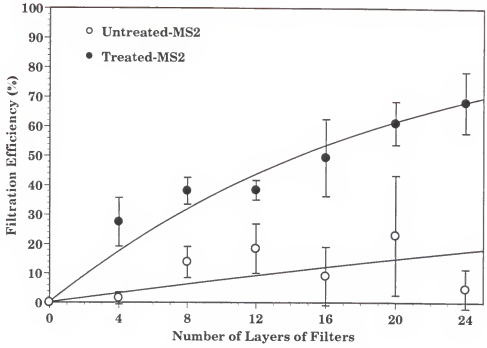


Figure 7-5. Filtration Efficiency of the uncoated and precipitated iron oxide coated polyester filters in the filtration of bacteriophage MS2.

Table 7-2. Filter coefficients, coefficients of linear regression, and filter coefficient improvements of the precipitated iron oxide coated polyester filters in the filtration of bacteriophages.

	MS2		PRD-1		ΦX-174	
	λ	R^2	λ	R^2	λ	R^2
Untreated Filter	0.008	0.23	0.005	0.46	0.005	0.59
Treated Filter	0.048	0.92	0.033	0.93	0.080	0.83
Improvement	500%	--	516%	--	1,388%	--

Table 7-3. Comparison of the filter coefficient improvements of the controlled goethite coating and the uncontrolled precipitated iron oxide coating.

Coating	*S. aureus*	*E. coli*	MS2	PRD-1	ΦX-174
Goethite	22%	36%	369%	506%	985%
Uncontrolled Precipitation	18%	-5%	500%	516%	1,388%

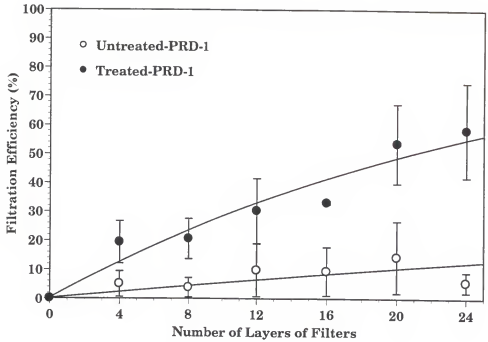


Figure 7-6. Filtration Efficiency of the uncoated and precipitated iron oxide coated polyester filters in the filtration of bacteriophage PRD-1.

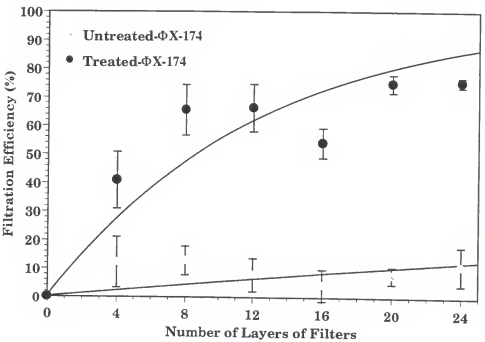


Figure 7-7. Filtration Efficiency of the uncoated and precipitated iron oxide coated polyester filters in the filtration of bacteriophage ΦX-174.

increased its probability of colliding with the filter surface. Certainly, there may be other factors that could account for the observed trends. Specific virus-host or virus-surface interactions still needs a great deal of research. The increased wettability of the filter surface may allow short-range forces to play an important role in the virus adsorption phenomena as well.

7.5 Summary

Iron oxide or oxides were coated on polyester fabric filters by soaking the filters in ferric chloride solution and then precipitating the oxides with a strong ammonium hydroxide solution. The resulting oxides probably consisted of many different forms of iron oxides. The treated filter has an isoelectric point of 4.5. The pressure drop of the treated filters is lower than that of the untreated filters due to the increased in wettability of the treated filters.

Filtration of bacteria results indicate that the treated filters are not very effective. In the filtration of *S. aureus*, the filter coefficient improves by only 18%. In the filtration of *E. coli*, there is no improvement in the filter coefficient with the precipitated treatment. Results for the bacteriophage filtration, on the other hand, are very different. The treated filters have improvements in the filter coefficient of 500%, 516% and 1,388% in the filtration of MS2, PRD-1 and ΦX-174, respectively.

CHAPTER 8
STABILITY OF METAL OXIDE COATED SAND: A TESTBED STUDY

8.1 Introduction

As discussed in the introduction section of Chapter 5, metallic hydroxide treated sand and diatomaceous earth have been shown to increase the media's ability to adsorb microorganisms from water. To shorten the time required for treatment, an *in-situ* precipitation method of coating was developed by Farrah and co-workers in which the metallic hydroxides were formed directly on the surface of the media (Farrah and Preston, 1985, Farrah *et al.*, 1991, Lukasik *et al.*, 1996). With this method, a combination of metallic hydroxides can be deposited on the surface of the sand or other media. The combination of iron and aluminum hydroxides has been found to be more effective in removing microorganisms than the individual iron or aluminum hydroxide coating (Lukasik *et al.*, 1996). Surface charge interaction is hypothesized to be the primary contributor to the improvement in the biofiltration process.

Industrial application of these metallic hydroxide coated sand requires that the coating display some degree of long term stability. Although the coating of iron and aluminum hydroxides by *in situ* precipitation method has been shown to be stable on a laboratory scale, the long-term stability on a larger scale has not been explored. For this purpose, a group of graduate and undergraduate students from the Advanced Separation Processes thrust group of the National Science Foundation Engineering Research Center

for Particle Science & Engineering at the University of Florida designed and constructed a testbed column. [In addition to their own research projects, all student members of the Engineering Research Center (ERC) are required to participate and contribute to a group project, in this case, the testbed filtration unit. Results shown in this chapter were obtained with the help and cooperation of many graduate and undergraduate students.] This testbed filtration unit has the same features as commercial upflow moving bed filters (e.g., Dynasand, Parkson Corp., Ft. Lauderdale FL). The features of the testbed column are described in detail in a later section. The leaching (due to solubility) and attritioning (due to shearing and breakage of the coatings) of the coated sand as a function of time was studied by several methods, including inductively coupled plasma emission (ICP) elemental analysis, zeta potential measurement, and bacterial and viral adsorption properties.

8.2 Materials and Methods

The dimensions of the testbed filtration column are given in Figure 8-1. The column consists of a water-feed ring, a center tube, two triangular fins, and sampling ports. The feed ring consists of 0.25-inch holes facing downward so that sand will be not clog the holes. Because of this orientation, water initially enters the column in a downward flow, then flows upward through the sand in the column. The center tube is used to transport the sand to the top of the column. This is accomplished by injecting compressed air inside the center tube near the lower end. The air- flow creates a suction that carries both the sand and water from the bottom of the column to the top. Once the sand is at the top, it is ejected from the center tube and falls back down the column. As

the sand falls, water flows upward and removes the coatings that have come off the surface of the sand. The particulate-contaminated water is sent to a drain, while fresh water is fed to the column. The triangular fins are used to keep the center tube in position. They are made of plexiglass material. The sampling ports are made of 0.5-inch copper ball valves.

The Parkson sand was obtained from Oglebay Norton Industrial (Brady, TX) and used as received. The sand was coated with a combination of iron and aluminum hydroxides according to the procedures outlined in Lukasik *et al* (1996). Fifty pounds of metallic hydroxide coated sand was then homogenized and placed in the testbed filter. Water flowrate was based on the superficial velocity (6.6 cm/min) established by the Dynasand pilot filter and set at 1.2 liters/minute. The pH of the tap water varies between pH 8.0 to 9.0. Air flowrate in the center tube was set at 0.4 liter/minute. The air flowrate was established empirically to match the sand turnover rate, 4-6 times/day, of the Dynasand pilot filter.

For the stability of the coatings experiment, the column ran without the backwash section, i.e. no reject stream. For the first 11 days, a sample of approximately 1 liter of sand was taken from the two lower sampling ports every 48 hours. A 20-mesh sieve was used to rinse the sample. The sample was then homogenized to assure uniformity and 400 ml of the homogenized sample was stored in the refrigerator for later analysis. The remaining sample was returned to the column. From day 11 to day 36, a sample was taken according the described procedure every 72 hours. For the remaining days, a sample was taken every 500 hours.

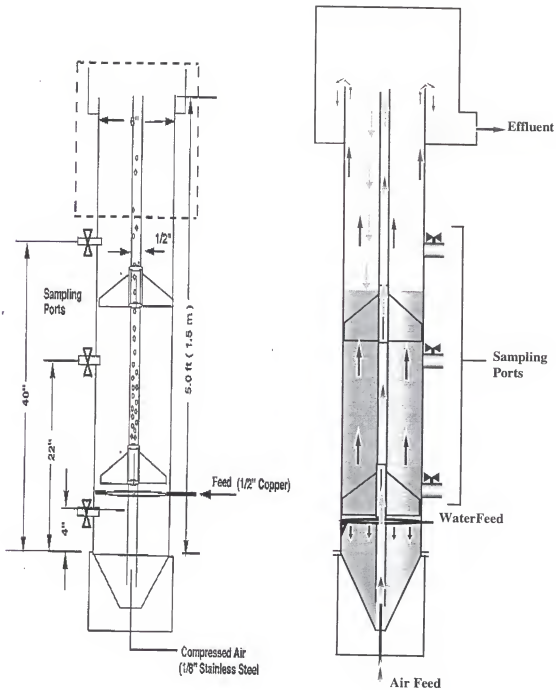


Figure 8-1. Schematic diagrams of the testbed filtration column.

A primary method of determining the longevity of the treated sand is to analyze the stability of the metals adsorbed on the sand surface. This was done by removing the

metal coating from a portion of the sample by dissolving it in hot acid. The concentration of the resulting solution was then measured using ICP elemental analysis. This number is then converted into the more useful units of [mg (metal)/g (sand)]. Three samples, weighing 20 grams each from each sand sample, were added to 100 ml of an acid solution made up of 20% (by volume) concentration hydrochloric acid, 40% concentrated nitric acid, and 40% deionized water. The mixture was heated until the boiling point is almost reached. The hot mixture was filtered and the sand was rinsed several times with deionized water. No residual metal coating on the sand was observed. The resulting solution was diluted to 1000 ml and the metal concentration was measured using ICP spectroscopy.

8.3 Microbial Preparation and Testing

Batch cultures of *Escherichia coli* C3000 (ATCC 15597) were grown overnight to early stationary phase in Nutrient Broth (Sigma) at 35°C with 120 rev min^{-1} shaking. Cells were harvested by centrifugation at 3000 × g for 10 min at 4°C, resuspended in filter-sterilized MilliQ water to $A_{550} = 0.40$, and stained with 4', 6-diamidino-2-phenyline-indole (DAPI) at a final concentration of 25 μg/ml for 30 min. Subsequently, cells were harvested and washed with artificial ground water (AGW) adjusted to pH 7.0, with centrifugation at 7000 × g for 10 min at 4°C, and then resuspended in AGW (pH 7.0) for use in batch or column removal tests. Suspensions of bacteriophages (MS2 and PRD-1) were prepared in AGW from refrigerated stocks kept in 3% tryptic soy broth (BBL) at pH 7.3. The microbial suspensions were kept at 4°C until use.

Batch removal tests with bacteria or phages were carried out using sand samples from the testbed column. In addition, unattritioned metallic oxide coated and uncoated sands were used as controls. Initial bacterial concentrations were 10^5-10^6 PFU/ml. Five grams of wet sand (rinsed with AGW) and 20 ml of suspension were used in the bacterial adsorption tests. Four grams of sand from the testbed filter or dry control sand were used with 10 ml of suspension in the bacteriophage adsorption tests. The test microbes were contacted with the respective sands in 50-ml plastic centrifuge tubes affixed to a 70 cm diameter wheel that was rotated vertically at 30 revolutions/minute at room temperature. The contact times were 2 hours for the bacteria and 30 minutes for the phages. Blanks containing microbial suspension but no sand were run along with the other tubes. At the end of the contacting time, the sand in the tubes was allowed to settle for 10 minutes at room temperature. Then the supernatants were sampled. The phage samples were immediately diluted in 1 % tryptic soy broth (TSB). Bacterial samples and phage dilutions were stored at 4°C until enumeration. All samples and controls were run in triplicate. The AGW has a pH of 7.0 and is buffered by bicarbonate.

Direct counts of bacterial samples were obtained within 48 hours (preliminary experiments showed that cell losses were 5% or less after this length of storage) using epifluorescence microscopy. The samples were not re-stained, hence only pre-stained cells were counted. This prevented interference from indigenous cells (background contamination or sloughed biomass). A Leitz microlab microscope, equipped with appropriate filter blocks for desired light excitation and emission, was used for visualization and counting. Samples were vortexed vigorously to mix well immediately before filtration. A 1.0-ml aliquot of sample was filtered through a sterile 0.20 μm pore

size, black, nucleation track polycarbonate filter (Nuclepore. Costar Scientific Corp.), with a 0.45 μm pore size membrane filter (GN-6, Gelman) placed underneath to evenly distribute the vacuum. Filters were pre-wetted with filter-sterilized MilliQ water and a vacuum of 600 mm Hg applied. Three milliliter of the filter-sterilized MilliQ water was added to the filter funnel immediately before applying vacuum to help disperse bacteria on the filter. Ten microscopic fields were counted per filter. Sample concentrations typically gave 25-50 cells per field.

Bacteriophages were assayed within 24 hours of sampling using the soft agar overlay method. Host bacteria (*Escherichia coli* for MS2, *Salmonella typhimurium* for PRD-1) were freshly grown in 3% TSB overnight at 37°C without agitation. Serial dilutions of phage samples were added in 0.1 ml aliquots to tubes containing 0.2 ml host bacteria. Then, 5 ml soft agar (40-45°C) was added to each tube, mixed, and poured while still warm onto plate count agar (DIFCO) containing 0.6 μg/ml of crystal violet. The plates were cooled for 5 min, incubated overnight (6-8 h) at 37°C, then plaques were counted.

8.4 Zeta Potential of the Metal Hydroxide Coated Sand

The zeta potential of the sand was determined using a homemade streaming potential apparatus (Figure 8-2). The apparatus consists of a flow-through cell packed with the sand being analyzed, tanks to provide electrolyte (0.1 mM KCl) solution, manometers to measure the pressure drop across the cell, electrodes placed at the edges of the packed bed within the sample cell, and a voltmeter (Keithley) to measure the electrical potential across the electrodes. The sample cell was constructed from clear

polycarbonate pipe, which allowed visual examination for air bubbles and uniformity of packing. Cell dimensions were 1.9 cm I.D. x 20.3 cm. The electrodes were 99% pure 18 gauge silver wire and 40 mesh size silver gauze (Newark Wire Cloth Co.) spot welded together so that the silver wire extended perpendicular from the center of the circular mesh. The mesh portion of an electrode was anodized in 0.1 mM HCl for 1 hour using a copper cathode with a 5 mA current. The finished electrode was treated in 1 mM KCl overnight to stabilize the silver chloride coating produced in the anodizing process.

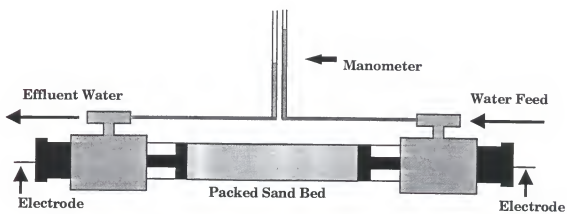


Figure 8-2. Streaming potential apparatus used to measure zeta potential of sand media.

Electrodes were regenerated or replaced every two to three weeks to ensure proper performance. Sand samples were packed into the sample cell by the tap and fill method. The packed bed was flushed with CO_2 to remove all the trapped air, then 1-2 L of 0.1 mM KCl electrolyte solution was allowed to flow through the bed to allow stable voltage measurements. The slope of the measured voltage versus pressure relationship along with

the measured solution conductivity was used to compute the zeta potential according to the following equation:

$$\zeta = \frac{4\pi\mu K}{\varepsilon\varepsilon_0}\frac{\Delta E}{\Delta P} \qquad (1)$$

where μ = viscosity of water, ε = dielectric constant of water, ε_0 = dielectric constant of a vacuum, K = conductivity, ΔP = hydrostatic pressure change, and ΔE = voltage change.

8.5 Results and Discussions

The amount of iron and aluminum coatings on the sand was analyzed using ICP spectroscopy. The results of these analyses are shown in Figure 8-3. After the treatment and a superficial rinsing, the iron content was determined to be 1.61 milligram per gram of sand and the aluminum content was 0.811 milligram per gram of sand. These results were significantly above the values for untreated sand, which were less than 0.02 milligram per gram of sand for iron and aluminum. After the sand was loaded into the column, both metals showed an initial period of rapid attritioning. After three days in the column, there was approximately a 35% decrease in the amount of iron on the sand. There was a corresponding 25% decrease in aluminum coating during the same time period. After this initial decrease, the rate of decline becomes much more gradual. Over the next 40 days, both the iron and aluminum decreased only 10% further, and remained significantly above the baseline values. From day 11 to day 22, the column was not operational.

From day 45 to day 96, the column was shut down again. During this down time, the sand in the column had to be removed twice in order to repair the center air tube. It is believed that these removals or handling of the sand caused the loss that was seen in Figure 8-3. The majority of the remaining metal content was removed during this second down period.

After the second down time, the coating again remained stable, although at a concentration much closer to the baseline value.

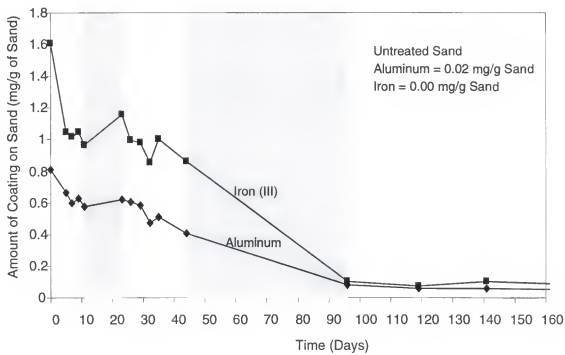


Figure 8-3. Attritioning and leaching of the metal coating on sand as a function of time

The zeta potential of particulate media, as measured by streaming potential, is another mean of tracking the longevity of the treatment. The zeta potential of the coated sand was measured throughout the run using the streaming potential instrument shown in Figure 8-2. Although the values never drop to the baseline value throughout the experiment, the reduction in zeta potential appears to follow the same trend as the other measured indicators. There was a very rapid decrease in its value during the first few days, followed by a slower rate of continued decline. By the end of the run, the measured value of the surface potential falls to about -80 mV, which is still above the baseline value (-95 mV).

The performance of the treated sand after attritioning in the test column was analyzed using batch bacterial (*E. coli*) tests. At each time interval, a sample from the untreated sand and the sand from the column were tested simultaneously to account for variations in the bacterial viability. This data is presented in Figure 8-5. There, again, appears to be a rapid decrease in performance during the first several days of exposure. A general downward progression in effectiveness continues over the whole of the run. This decrease in adsorption efficiency was correlated with the decrease in metal content and the increase in the electronegativity of the media. From day 140 to day 159, even though the adsorption efficiency is low, it is still above the value of the untreated sand, which indicates that the small amount of metal coating on the sand is still effective in removing the bacteria.

To evaluate the performance of the attritioned sand for bacteriophage removal, batch adsorption tests were conducted to measure the reduction of MS2 and PRD-1. This data is shown in Figure 8-6. For the duration of the run, the metal oxide treated sand consistently removed several times more phage than untreated sand. In the batch test, the untreated sand removed about 4% and 12% of the MS2 and PRD-1 phages, respectively. The initial unattritioned, treated sand significantly outperformed the untreated sand, removing about 43% of the MS2 and 68% of the PRD-1. In each case, the removal efficiency decreases with time. The decrease in removal efficiency was more gradual than other indicators such as metal content analysis. These results suggest that for the removal of bacteriophages, only a small amount of coating on the sand is necessary. The values remained above the untreated baseline even at the end of the run, at 14% and 43% for MS2 and PRD1, respectively.

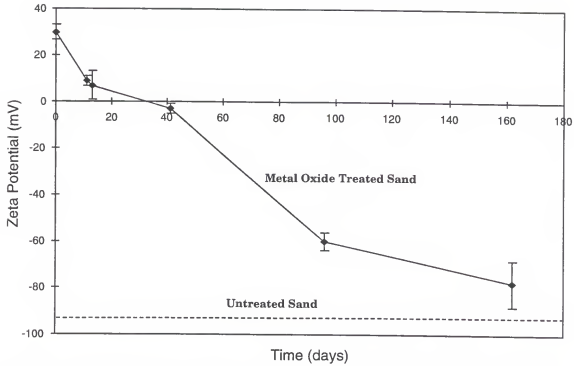


Figure 8-4. Zeta potential of the sand from the column as a function of time at pH 7.0.

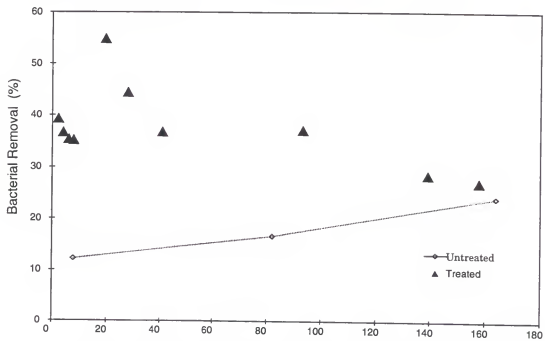


Figure 8-5. Batch bacterial removal results for the sand as a function of time.

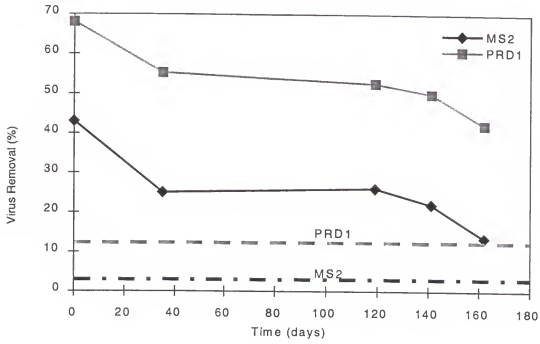


Figure 8-6. Batch removal of Bacteriophages as function of column run-time.

8.6 Summary

Since sand coated with iron and aluminum oxide mixture has been shown to be effective in the removal of bacteria and bacteriophages on the laboratory scale, a testbed filtration unit was constructed to determine the stability and industrial applicability of the coated Parkson sand. This testbed filtration unit has the same features as commercial upflow moving bed filters (e.g., Dynasand, Parkson Corp., Ft. Lauderdale FL). Results of the coating stability study shows that there was an initial period of rapid attritioning, followed by more gradual loss of coating. The iron and aluminum hydroxide coated sand is more effective than untreated sand in the removal of both bacterial and viral contaminants over any given time period. Reduced concentrations of metal hydroxide on the surface can be correlated to the decreased in filtration efficiency of both bacteria and

bacteriophages. This reduction in concentration asymptotically approaches the value of the untreated sand. The sand coating remained an effective filtration enhancement after at least 90 days in the continuous filter.

CHAPTER 9
CONCLUSIONS AND FUTURE WORK

9.1 Conclusions

Microporous polypropylene filters and microdenier polyester textile fabric filters were modified with a cationic surfactant and metal oxides/hydroxides. These treated filters were then used to filter negatively charged nanoparticles and biological particles such as bacteria and viruses.

The microporous polypropylene filters were modified with a two-tailed cationic surfactant, dimethyldioctadecylammonium bromide (DDAB), to create a positively charged surface. Negatively charged particles can then be filtered by utilizing the electrostatic interaction between the charged particles and the polar heads of the surfactants adsorbed on the filters. Filtration results for 60 nm negatively charged particles (carboxylate-modified copolymer) filtered through DDAB treated microporous polypropylene filters show a four to five fold increase in particle filtration efficiency. Filtration efficiency was found to be dependent on the solution pH and the pore size of the filters. Multiple layers of filters can boost the filtration efficiency up to 95 percent with only 4 layers of filters. Thus, the results of this study clearly established the importance of surface modification of filters to enhance filtration efficiency by enhancing the attractive Coulombic interaction between the nanoparticles and the filter surface.

To compare the metal oxide coatings with the surfactant coatings, surfactants were used to coat microdenier polyester textile fabric filters. Polyester was used because the melt-blown polypropylene filters were not strong enough to withstand the mechanical agitation in metal oxide coating process. Filtration results show that the filter coefficient of the surfactant treated polyester filters improves by 195% and 330% in the filtration of *S. aureus* and *E. coli*, respectively. To show that the surfactant treated filter surface is more active, untreated and surfactant treated polyester filters were soaked in a concentrated solution of bacteria for 30 minutes. SEM pictures show that the surface of the surfactant treated filter did indeed absorb significantly more bacteria than the surface of the untreated filter. In the filtration of bacteriophages, the improvements in the filter coefficient of the surfactant treated filters are 3,270%, 2,830% and 98% in the filtration of MS2, PRD-1 and ΦX-174, respectively. The poor result for the ΦX-174 filtration is attributed to its high isoelectric point. At the experimental condition, it is the least negatively charged. Similar to the nanoparticle filtration results, these bacteria and bacteriophage filtration results provide convincing evidence that surface modification based on electrostatic interaction can greatly improve the filtration efficiency of the modified filters.

Three different forms of iron oxides were successfull coated on polyester fabric filters. The oxides are goethite, haematite, and magnetite. The iron oxide coated filters have zeta potentials that are less negatively charged that the untreated filters, but they are still negatively charged. The coatings make the filters very wettable, and therefore, the pressure drop across the filters is drastically reduced. In the filtration of bacteria, the iron oxide coated filters show some improvements in filtration efficiency. Compared to the

uncoated filters, the filter coefficients of the goethite, haematite and magnetite coated filters have improvements of 22%, 60% and 53%, respectively, in the filtration of *S. aureus*. In the filtration of *E. coli*, the filter coefficient improvements are 36%, 45% and 51% for goethite, haematite and magnetite coatings, respectively. While the efficiencies of the iron oxide coated filters are higher than the untreated filters, they are far less efficient than the surfactant treated filters in the filtration of bacteria.

In the filtration of bacteriophages, the goethite shows some promise for the filtration of MS2 and PRD-1. Haematite and magnetite are not effective in the filtration of MS2 and PRD-1. In the filtration of ΦX-174, the results are very promising. The improvements in filter coefficients are 985%, 1,035% and 406% for goethite, haematite and magnetite coated filters, respectively. At this point, it is unclear as to why these oxide surfaces are very effective in removing phage ΦX-174. These results suggest that factors other than electrostatic interaction may be just as important in the adhesion or adsorption of some of the microorganisms. These factors may involve specific-interactions such as those exhibited by the bacteriophages in their selective attachment to their hosts.

Mixed oxides of iron and aluminum were also coated on polyester fabric filters. The four different mixed oxide coated filters has 25, 50, 75, and 100 mole% of aluminum in the formulation. The coated filters show positive zeta potentials in acidic pH and changes to negative as the pH increases. All of the isoelectric points of the mixed oxide coated filters are between 6 and 7. Out of the mixed oxide coated filters, the 75% Al sample is the most electronegative at pH 7, the experimental condition. The 25% Al, 50% Al, and 100% Al oxide coated filters have very similar filtration efficiencies for both

bacteria. With the exception of the 75% Al coated filters, the mixed oxide coated filters have filter coefficient improvements ranging from 111% to 130% in the filtration of *S. aureus* and 169% to 183% in the filtration of *E. coli*. The 75% Al mixed oxide coated filters has improvements of only 63% in the filtration of *S. aureus* and 70% in the filtration of *E. coli*. Similar to the filtration of bacteria, the 25% Al, 50% Al and 100% Al coated filters have identical filtration efficiencies. The 75% Al coated filters has the worst performance out the mixed oxide coated filters. In the filtration of MS2, the improvements range from 1,600% to 2,100% for the 25% Al, 50% Al and 100% Al coated filters. In the filtration of PRD-1, the improvements for the same three filters range from 1,700% to 1,900%. The same three filters have slightly better improvements of 1,800% to 2,300% in the filtration of ΦX-174. In both the filtration of bacteria and bacteriophages, the mixed oxides are much more effective than the iron oxides. The improvement of the mixed oxides over the iron oxides has a strong correlation with the decrease in the electronegativity of the mixed oxide treated filters. The effectiveness of the mixed oxide coated filters is comparable to that of the surfactant treated filters. In the filtration of phage ΦX-174, the mixed oxides have the highest efficiency of all the different coatings.

9.2 Future Work

Wettability. In the filtration of bacteriophages with the metal oxide coated filters, the increased wettability of the treated filter surface may be an important parameter in the phage adsorption/adhesion process. To elucidate the affect of wettability on the adhesion process, one of the best ways is to treat the polyester filters with polyvinyl alcohol (PVA)

since PVA is known to make materials very wettable. The treated filters can then be used to filter bacteria and bacteriophages.

Metal Oxides. Only three forms of iron oxides out the sixteen various iron oxides were examined for their bacterial and viral removal properties. It may be worthwhile to examine other oxides besides goethite, haematite, and magnetite. With the aluminum and iron oxide mixtures, the ratio of 75% mole percent aluminum was found to be detrimental to the filtration efficiency of the filters. From the SEM pictures, the structure of the coating is different from all of the other mixtures. The structure may be an indication of a different form of aluminum oxide. Similar to iron oxides, aluminum oxides can have different morphologies as well. The different forms of aluminum oxides were not discussed or tested in this study. By isolating the different forms of aluminum oxides, one may find that certain oxides will perform better than others in the filtration process.

Polymer Surface Modifications. While the modifications described above, such as the metal oxide coatings, are suitable for large-scale sand filtration processes, they may not be the best solution for smaller scale processes or uses. For household use, for example, since the filter is the final step, other permanent type of modifications might be better suited to these applications. Although the metal oxide coatings are fairly stable, they will, to some extent, attrition off the filter and end up in the filtrate. Modifications of the polymers used to make the filters with plasma treatment, for example, should be investigated. Functionalized siloxane polymers should also be explored.

APPENDIX A
ZETA POTENTIAL (STREAMING POTENTIAL) APPARATUS

Streaming potential is the potential created when a fluid is made to flow passed a charged stationary phase. By measuring the streaming potential and the associated pressure drop (proportional to the flowrate), one can calculate the zeta potential. A streaming potential apparatus was constructed for the measurement of the zeta potential of the filter media used in this work. The apparatus is shown in Figure 1-1. The apparatus consists of a flow-through cell packed with six layers of filters, tanks to provide electrolyte (0.01 mM KCl) flow through the cell, manometers to measure the pressure drop across the cell, electrodes placed at the edges of the packed bed within the sample cell, and a voltmeter (Keithley) to measure the electrical potential across the electrodes. The sample cell was made from precision-bore glass, and the silver electrodes were purchased from Brookhaven Instruments Corporation (Holtsville, NY). Flowrate or pressure drop was controlled by adjusting the height of the flow inlet and outlet. Flowrate was kept at a very slow rate to insure that the flow through the filters was laminar flow.

To calculate the zeta potential fo the filters, the pressure drop was manipulated to have 8 different values and the corresponding voltage was recorded. The data were then plotted and the slope of the measured voltage versus pressure relationship along with the

measured solution conductivity was used to compute the zeta potential according to the following equation.

$$\zeta = \frac{4\pi\mu K}{\varepsilon\varepsilon_0}\frac{\Delta E}{\Delta P}$$

where μ = viscosity of water, ε = dielectric constant of water, ε_0 = dielectric constant of a vacuum, K = conductivity, ΔP = hydrostatic pressure difference, and ΔE = voltage change.

All reported values in the following chapters are averages of three separate measurements. For measurement at different pH values, approximately 4 liters of the solution was allowed to flow through the filters to achieve equilibrium conditions.

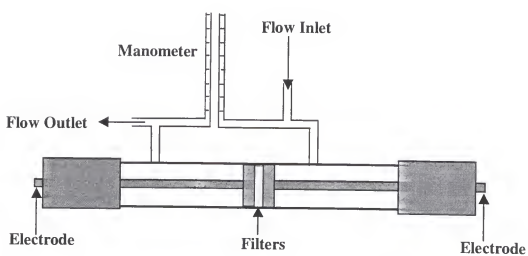
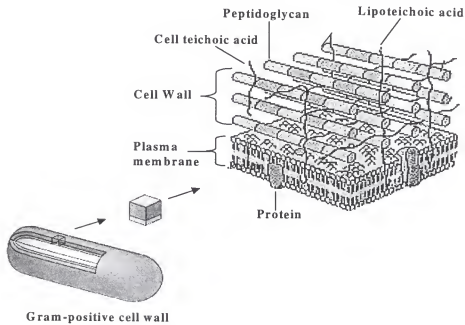
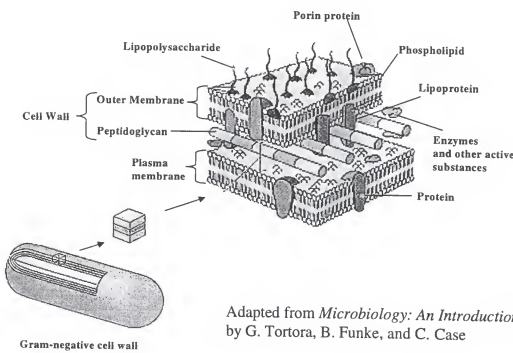


Figure 1-1. Schematic illustration of streaming potential apparatus for measuring zeta potential of fibrous materials.

APPENDIX B
STRUCTURE OF GRAM-POSITIVE AND GRAM-NEGATIVE BACTERIA





Adapted from *Microbiology: An Introduction* by G. Tortora, B. Funke, and C. Case

APPENDIX C
STABILILTY OF IRON OXIDE COATINGS

For filtration applications, stability of the iron oxide coatings is very important. To determine the longevity of these coatings, the iron oxide coated polyester filters were flushed with deionized water. Two filter holders were connected in series, each having four layers of filters. The flowrate was approximately 150 ml/minute.

After 650 L of water has passed through the filters, concentrated hydrochloric acid was used to dissolve the iron coating from the polyester filters. The solution was then analyzed using ICP. The results are shown in the following Table C. For the goethite coated filters, the untreated filters have 4.06 mg of iron per filter before they were flushed with deionized water. After 650 L of flushing, the filters contain 4.58 mg of iron per filter. Although this number is slightly higher than the unrinsed samples, the difference is probably due to variations from sample to sample. For the haematite and magnetite coated filters, there is no loss in the amount of coating on the filters. These results show that the iron oxide coatings are very stable.

Table C. Amount of iron on filter before and after rinsing or flushing with 650 L of deionized water.

Sample	No Rinse (mg/filter)	650 L of Rinse (mg/filter)
Untreated	0.03	0.07
Goethite	4.06	4.58
Haematite	5.72	5.77
Magnetite	3.72	3.67

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BIOGRAPHICAL SKETCH

Peter Kea Kang was born on February 2, 1970, in Cambodia. He and his family escaped from Cambodia under the cover of darkness and entered a refugee camp in Thailand in 1979. After spending 2 years in the refugee camp, they immigrated to the United States in September 1981. He graduated from high school in Doraville, GA, in 1989, as the salutatorian. He continued his studies at Georgia Institute of Technology where he obtained his Bachelor's degree in Chemical Engineering in June of 1994. While a student at GA Tech, Peter worked with Dow Chemical for one and one half years as a co-op student.

In August of 1994, he started his graduate studies under the supervision of Dr. Dinesh O. Shah in the Chemical Engineering Department at the University of Florida. He is also a member of the National Science Foundation Engineering Research Center for Particle Science & Technology at the University of Florida.

Highlights of his academic accomplishments include two patent disclosures, one with the University of Florida and one with Milliken Research Corporation. He also won first prize award in the 1994 American Institute of Chemical Engineers National Student Design Competition.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Dinesh O. Shah, Chairman
Professor of
Chemical Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Hassan El-Shall
Engineer
Material Science and Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Ben Koopman
Professor of
Environmental Engineering Sciences

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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Associate Professor of
Chemical Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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This dissertation was submitted to the Graduate Faculty of the College of Engineering and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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